Connecting via Winsock to STN

Welcome to STN International! Enter x:x

LOGINID:SSSPTA1626GMS

PASSWORD:
TERMINAL (ENTER 1, 2, 3, OR ?):2

* * * * * * * * * * Welcome to STN International * * * * * * * * * *

NEWS 1		Web Page URLs for STN Seminar Schedule - N. America
NEWS 2		"Ask CAS" for self-help around the clock
NEWS 3	JAN 17	Pre-1988 INPI data added to MARPAT
NEWS 4	FEB 21	STN AnaVist, Version 1.1, lets you share your STN AnaVist visualization results
NEWS 5	FEB 22	The IPC thesaurus added to additional patent databases on STN
NEWS 6	FEB 22	Updates in EPFULL; IPC 8 enhancements added
NEWS 7	FEB 27	New STN AnaVist pricing effective March 1, 2006
NEWS 8	MAR 03	Updates in PATDPA; addition of IPC 8 data without attributes
NEWS 9	MAR 22	EMBASE is now updated on a daily basis
NEWS 10	APR 03	New IPC 8 fields and IPC thesaurus added to PATDPAFULL
NEWS 11	APR 03	Bibliographic data updates resume; new IPC 8 fields and IPC thesaurus added in PCTFULL
NEWS 12	APR 04	STN AnaVist $500 visualization usage credit offered
NEWS 13	APR 12	LINSPEC, learning database for INSPEC, reloaded and enhanced
NEWS 14	APR 12	Improved structure highlighting in FQHIT and QHIT display in MARPAT
NEWS 15	APR 12	Derwent World Patents Index to be reloaded and enhanced during second quarter; strategies may be affected
NEWS 16	MAY 10	CA/CAplus enhanced with 1900-1906 U.S. patent records
NEWS 17	MAY 11	KOREAPAT updates resume
NEWS 18	MAY 19	Derwent World Patents Index to be reloaded and enhanced
NEWS 19	MAY 30	IPC 8 Rolled-up Core codes added to CA/CAplus and USPATFULL/USPAT2
NEWS 20	MAY 30	The F-Term thesaurus is now available in CA/CAplus
NEWS 21	JUN 02	The first reclassification of IPC codes now complete in INPADOC

NEWS EXPRESS FEBRUARY 15 CURRENT VERSION FOR WINDOWS IS V8.01a, CURRENT MACINTOSH VERSION IS V6.0c(ENG) AND V6.0Jc(JP), AND CURRENT DISCOVER FILE IS DATED 19 DECEMBER 2005. V8.0 AND V8.01 USERS CAN OBTAIN THE UPGRADE TO V8.01a AT http://download.cas.org/express/v8.0-Discover/

NEWS HOURS	STN Operating Hours Plus Help Desk Availability
NEWS LOGIN	Welcome Banner and News Items
NEWS IPC8	For general information regarding STN implementation of IPC 8
NEWS X25	X.25 communication option no longer available after June 2006

Enter NEWS followed by the item number or name to see news on that specific topic.

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* * * * * * * * * * * * * * * * STN Columbus * * * * * * * * * * * * * * * *

FILE 'HOME' ENTERED AT 09:41:13 ON 07 JUN 2006

=>
Uploading
THIS COMMAND NOT AVAILABLE IN THE CURRENT FILE
Do you want to switch to the Registry File?
Choice (Y/n):
Switching to the Registry File...
Some commands only work in certain files. For example, the EXPAND command can only be used to look at the index in a file which has an index. Enter "HELP COMMANDS" at an arrow prompt (=>) for a list of commands which can be used in this file.

=> FILE REGISTRY

COST IN U.S. DOLLARS	SINCE FILE ENTRY	TOTAL SESSION
FULL ESTIMATED COST	0.21	0.21

FILE 'REGISTRY' ENTERED AT 09:41:24 ON 07 JUN 2006
USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.
PLEASE SEE "HELP USAGETERMS" FOR DETAILS.

Property values tagged with IC are from the ZIC/VINITI data file provided by InfoChem.

STRUCTURE FILE UPDATES: 6 JUN 2006 HIGHEST RN 887000-62-6
DICTIONARY FILE UPDATES: 6 JUN 2006 HIGHEST RN 887000-62-6

New CAS Information Use Policies, enter HELP USAGETERMS for details.

TSCA INFORMATION NOW CURRENT THROUGH January 6, 2006

Please note that search-term pricing does apply when conducting SmartSELECT searches.

****
* *
* The CA roles and document type information have been removed from *
* the IDE default display format and the ED field has been added, *
* effective March 20, 2005. A new display format, IDERL, is now *
* available and contains the CA role and document type information. *
* *
****

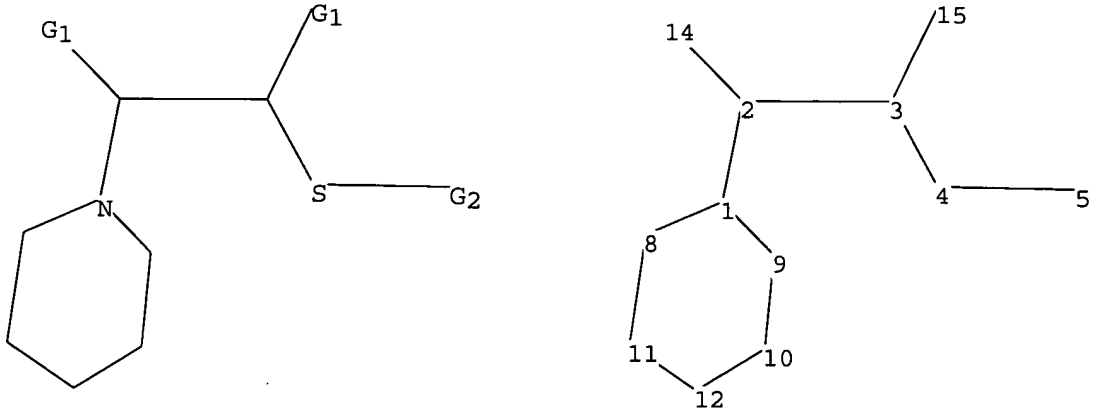
Structure search iteration limits have been increased. See HELP SLIMITS for details.

REGISTRY includes numerically searchable data for experimental and predicted properties as well as tags indicating availability of experimental property data in the original document. For information

on property searching in REGISTRY, refer to:

http://www.cas.org/ONLINE/UG/regprops.html

=>
Uploading C:\Program Files\Stnexp\Queries\10807710c.str



chain nodes :
2 3 4 5 14 15
ring nodes :
1 8 9 10 11 12
chain bonds :
1-2 2-3 2-14 3-4 3-15 4-5
ring bonds :
1-8 1-9 8-11 9-10 10-12 11-12
exact/norm bonds :
1-2 1-8 1-9 2-14 3-4 3-15 4-5 8-11 9-10 10-12 11-12
exact bonds :
2-3
isolated ring systems :
containing 1 :

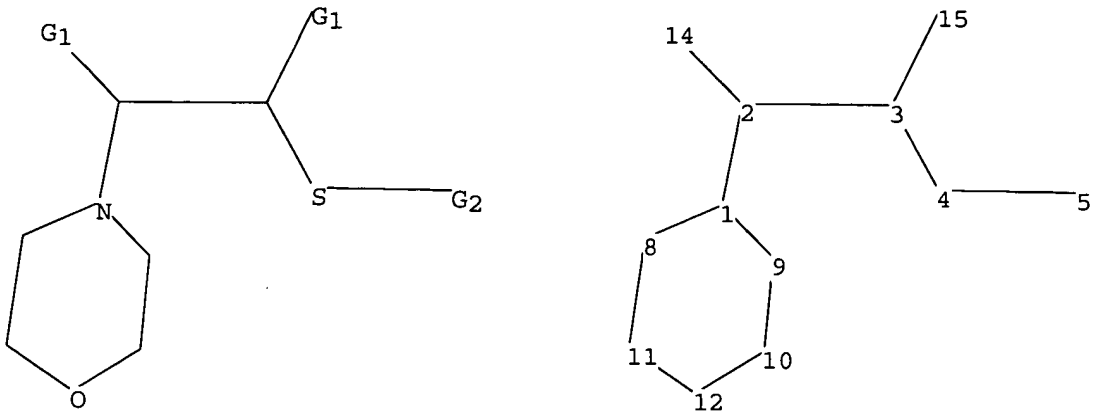
G1:Ak,Ph,Cb,Cy

G2:H,CH3

Match level :
1:CLASS 2:CLASS 3:CLASS 4:CLASS 5:CLASS 8:CLASS 9:CLASS 10:CLASS 11:CLASS
12:CLASS 14:CLASS 15:CLASS

L1 STRUCTURE UPLOADED

=> d l1
L1 HAS NO ANSWERS
L1 STR



chain nodes :
2 3 4 5 14 15
ring nodes :
1 8 9 10 11 12
chain bonds :
1-2 2-3 2-14 3-4 3-15 4-5
ring bonds :
1-8 1-9 8-11 9-10 10-12 11-12
exact/norm bonds :
1-2 1-8 1-9 2-14 3-4 3-15 4-5 8-11 9-10 10-12 11-12
exact bonds :
2-3
isolated ring systems :
containing 1 :

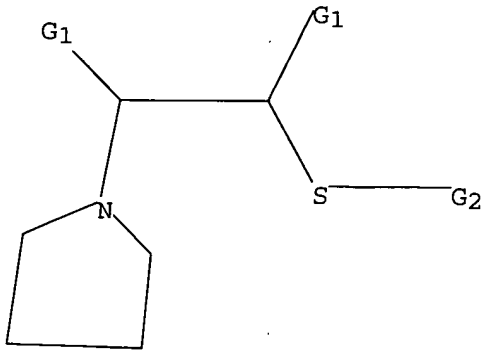
G1:Ak,Ph,Cb,Cy

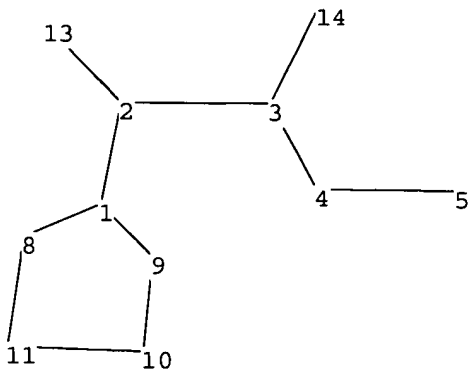
G2:H,CH3

Match level :
1:CLASS 2:CLASS 3:CLASS 4:CLASS 5:CLASS 8:CLASS 9:CLASS 10:CLASS 11:CLASS
12:CLASS 14:CLASS 15:CLASS

L4 STRUCTURE UPLOADED

=> d l4
L4 HAS NO ANSWERS
L4 STR





chain nodes :
2 3 4 5 13 14
ring nodes :
1 8 9 10 11
chain bonds :
1-2 2-3 2-13 3-4 3-14 4-5
ring bonds :
1-8 1-9 8-11 9-10 10-11
exact/norm bonds :
1-2 1-8 1-9 2-13 3-4 3-14 4-5
exact bonds :
2-3 8-11 9-10 10-11
isolated ring systems :
containing 1 :

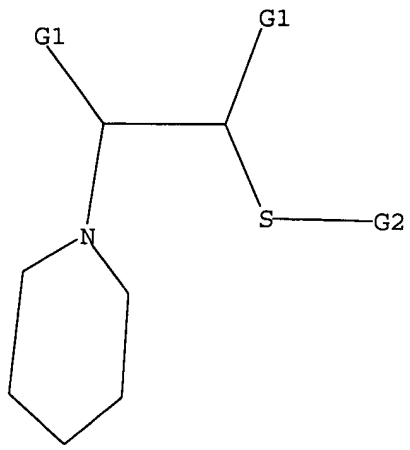
G1:Ak,Ph,Cb,Cy

G2:H,CH3

Match level :
1:CLASS 2:CLASS 3:CLASS 4:CLASS 5:CLASS 8:CLASS 9:CLASS 10:CLASS 11:CLASS
13:CLASS 14:CLASS

L7 STRUCTURE UPLOADED

=> d l7
L7 HAS NO ANSWERS
L7 STR



G1 Ak,Ph,Cb,Cy
G2 H,Me

Structure attributes must be viewed using STN Express query preparation.

```
=> s l1
SAMPLE SEARCH INITIATED 09:41:55 FILE 'REGISTRY'
SAMPLE SCREEN SEARCH COMPLETED -     3999 TO ITERATE

 50.0% PROCESSED     2000 ITERATIONS                                  2 ANSWERS
INCOMPLETE SEARCH (SYSTEM LIMIT EXCEEDED)
SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS:  ONLINE  **COMPLETE**
                        BATCH   **COMPLETE**
PROJECTED ITERATIONS:        76188 TO    83772
PROJECTED ANSWERS:               2 TO      198

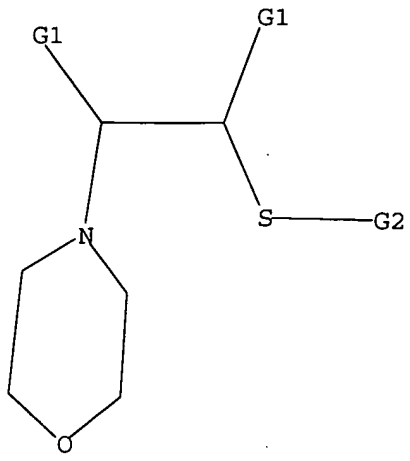
L2            2 SEA SSS SAM L1

=> s l1 sss full
FULL SEARCH INITIATED 09:42:02 FILE 'REGISTRY'
FULL SCREEN SEARCH COMPLETED -    78029 TO ITERATE

100.0% PROCESSED    78029 ITERATIONS                                 23 ANSWERS
SEARCH TIME: 00.00.04

L3            23 SEA SSS FUL L1

=>
Uploading C:\Program Files\Stnexp\Queries\10807710d.str
```



G1 Ak,Ph,Cb,Cy
G2 H,Me

Structure attributes must be viewed using STN Express query preparation.

```
=> s l4
SAMPLE SEARCH INITIATED 09:43:35 FILE 'REGISTRY'
SAMPLE SCREEN SEARCH COMPLETED -      681 TO ITERATE

100.0% PROCESSED      681 ITERATIONS                                0 ANSWERS
SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS:  ONLINE  **COMPLETE**
                        BATCH   **COMPLETE**
PROJECTED ITERATIONS:        12055 TO    15185
PROJECTED ANSWERS:               0 TO        0

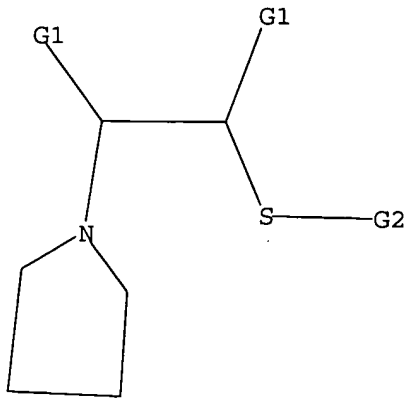
L5            0 SEA SSS SAM L4

=> s l4 sss full
FULL SEARCH INITIATED 09:43:41 FILE 'REGISTRY'
FULL SCREEN SEARCH COMPLETED -    13496 TO ITERATE

100.0% PROCESSED    13496 ITERATIONS                     23 ANSWERS
SEARCH TIME: 00.00.01

L6           23 SEA SSS FUL L4

=>
Uploading C:\Program Files\Stnexp\Queries\10807710e.str
```



G1 Ak,Ph,Cb,Cy
G2 H,Me

Structure attributes must be viewed using STN Express query preparation.

```
=> s l7
SAMPLE SEARCH INITIATED 09:44:59 FILE 'REGISTRY'
SAMPLE SCREEN SEARCH COMPLETED -     3687 TO ITERATE

 54.2% PROCESSED     2000 ITERATIONS                                  0 ANSWERS
INCOMPLETE SEARCH (SYSTEM LIMIT EXCEEDED)
SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS:  ONLINE  **COMPLETE**
                        BATCH   **COMPLETE**
PROJECTED ITERATIONS:        70099 TO    77381
PROJECTED ANSWERS:               0 TO        0

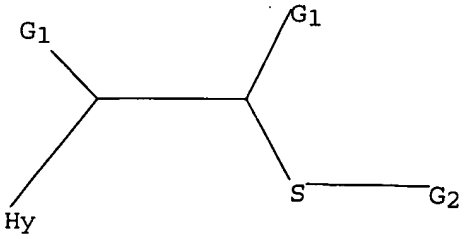
L8             0 SEA SSS SAM L7

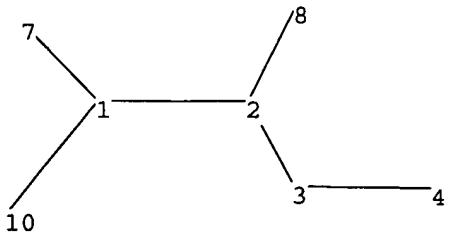
=> s l7 sss full
FULL SEARCH INITIATED 09:45:06 FILE 'REGISTRY'
FULL SCREEN SEARCH COMPLETED -    73630 TO ITERATE

100.0% PROCESSED    73630 ITERATIONS                     19 ANSWERS
SEARCH TIME: 00.00.02

L9            19 SEA SSS FUL L7

=>
Uploading C:\Program Files\Stnexp\Queries\10807710f.str
```





chain nodes :
1 2 3 4 7 8 10
chain bonds :
1-7 1-2 1-10 2-3 2-8 3-4
exact/norm bonds :
1-7 1-10 2-3 2-8 3-4
exact bonds :
1-2

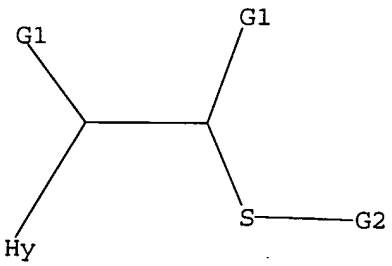
G1:Ak,Ph,Cb,Cy

G2:H,CH3

Match level :
1:CLASS 2:CLASS 3:CLASS 4:CLASS 7:CLASS 8:CLASS 10:Atom

L10 STRUCTURE UPLOADED

=> d l10
L10 HAS NO ANSWERS
L10 STR



G1 Ak,Ph,Cb,Cy
G2 H,Me

Structure attributes must be viewed using STN Express query preparation.

=> s l10
SAMPLE SEARCH INITIATED 09:47:09 FILE 'REGISTRY'
SAMPLE SCREEN SEARCH COMPLETED - 215607 TO ITERATE

0.9% PROCESSED 2000 ITERATIONS 0 ANSWERS
INCOMPLETE SEARCH (SYSTEM LIMIT EXCEEDED)
SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS: ONLINE **INCOMPLETE**
BATCH **INCOMPLETE**
PROJECTED ITERATIONS: 4284985 TO 4339295
PROJECTED ANSWERS: 0 TO 0

L11 0 SEA SSS SAM L10

```
=> s l10 sss full
FULL SEARCH INITIATED 09:47:16 FILE 'REGISTRY'
FULL SCREEN SEARCH COMPLETED -  4317647 TO ITERATE

 14.3% PROCESSED   619487 ITERATIONS                          38 ANSWERS

 22.7% PROCESSED   979860 ITERATIONS                          50 ANSWERS

 23.2% PROCESSED  1000000 ITERATIONS                          57 ANSWERS
INCOMPLETE SEARCH (SYSTEM LIMIT EXCEEDED)
SEARCH TIME: 00.00.33

FULL FILE PROJECTIONS:  ONLINE  **INCOMPLETE**
                        BATCH   **INCOMPLETE**
PROJECTED ITERATIONS:      4317647 TO  4317647
PROJECTED ANSWERS:             199 TO      293

L12          57 SEA SSS FUL L10

=> FIL HCAPLUS
COST IN U.S. DOLLARS                          SINCE FILE      TOTAL
                                                 ENTRY    SESSION
FULL ESTIMATED COST                             670.84     671.05

FILE 'HCAPLUS' ENTERED AT 09:47:56 ON 07 JUN 2006
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FILE COVERS 1907 - 7 Jun 2006  VOL 144 ISS 24
FILE LAST UPDATED: 6 Jun 2006  (20060606/ED)

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 This file contains CAS Registry Numbers for easy and accurate
 substance identification.

=> d his

     (FILE 'HOME' ENTERED AT 09:41:13 ON 07 JUN 2006)

     FILE 'REGISTRY' ENTERED AT 09:41:24 ON 07 JUN 2006
L1             STRUCTURE UPLOADED
L2           2 S L1
L3          23 S L1 SSS FULL
L4             STRUCTURE UPLOADED
L5           0 S L4
```

```
L6            23 S L4 SSS FULL
L7                STRUCTURE UPLOADED
L8             0 S L7
L9            19 S L7 SSS FULL
L10               STRUCTURE UPLOADED
L11            0 S L10
L12           57 S L10 SSS FULL

     FILE 'HCAPLUS' ENTERED AT 09:47:56 ON 07 JUN 2006

=> s l3
L13           24 L3

=> s l6
L14            9 L6

=> s l9
L15           12 L9

=> s l12
L16           20 L12

=> s l13 and py<=2002
      22805773 PY<=2002
L17           19 L13 AND PY<=2002

=> d l13 ibib abs hitstr tot

L13  ANSWER 1 OF 24  HCAPLUS  COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER:         2005:354977  HCAPLUS
DOCUMENT NUMBER:          142:463603
TITLE:                    Aminoethanethiol derivatives as highly efficient
                          chiral ligands in asymmetric reactions, especially in
                          enantioselective nucleophilic addition of carbonyls
                          with alkylmetals
INVENTOR(S):              Yang, Denggui; Liu, Ta; Chen, Nanguang
PATENT ASSIGNEE(S):       Haimen Huiju Pharmaceutical Co., Ltd., Peop. Rep.
                          China
SOURCE:                   Faming Zhuanli Shenqing Gongkai Shuomingshu, 9 pp.
                          CODEN: CNXXEV
DOCUMENT TYPE:            Patent
LANGUAGE:                 Chinese
FAMILY ACC. NUM. COUNT:   1
PATENT INFORMATION:

     PATENT NO.           KIND   DATE        APPLICATION NO.         DATE
     ---------------      ----   ----------  --------------------    --------
     CN 1434034            A     20030806    CN 2001-143059          20011207
PRIORITY APPLN. INFO.:                       CN 2001-143059          20011207
OTHER SOURCE(S):          CASREACT 142:463603
GI
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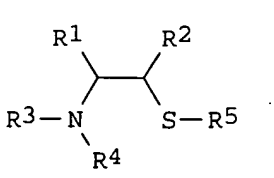
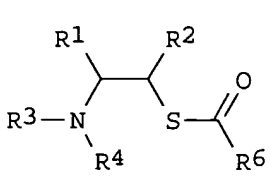
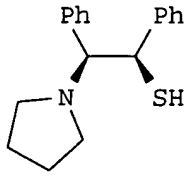


I



II



III

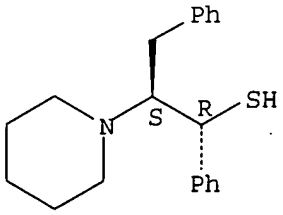
AB The invention relates to aminoethanethiol derivs. I and II [wherein R1, R2 = alkyl or aryl; R3, R4 = alkyl; R5, R6 = H or alkyl; etc.] and their applications as chiral ligands in asym. reactions, especially in asym. reduction of aldehydes through their organometallic (Zn, Cu and Ti) complexes and in enantioselective nucleophilic addition of carbonyl compds. with alkylmetals. The remarkably high asym.-induction efficiency of the invented compds. were demonstrated by three examples such as III using addition reaction of benzaldehyde with diethylzinc as probe. As little as 0.02% (molar ratio of ligand to substrate) of the ligands were enough to achieve >99% ee.

IT **851474-77-6**
RL: CAT (Catalyst use); USES (Uses)
(aminoethanethiol derivs. as highly efficient chiral ligands in asym. reactions)

RN 851474-77-6 HCAPLUS

CN 1-Piperidineethanethiol, α-phenyl-β-(phenylmethyl)-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



L13 ANSWER 2 OF 24 HCAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 2005:130245 HCAPLUS

DOCUMENT NUMBER: 142:373291

TITLE: New β-amino thiols as efficient catalysts for highly enantioselective alkenylzinc addition to aldehydes

AUTHOR(S): Tseng, Shi-Liang; Yang, Teng-Kuei

CORPORATE SOURCE: Department of Chemistry, National Chung-Hsing University, Taichung, 40227, Peop. Rep. China

SOURCE: Tetrahedron: Asymmetry (2005), 16(4), 773-782
CODEN: TASYE3; ISSN: 0957-4166

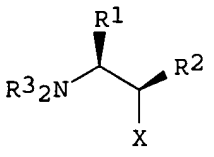
PUBLISHER: Elsevier B.V.

DOCUMENT TYPE: Journal

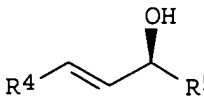
LANGUAGE: English

OTHER SOURCE(S): CASREACT 142:373291

GI



I



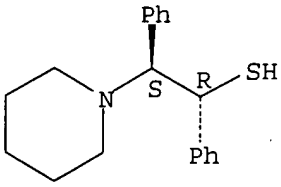
II

AB A series of new optically active β-amino thiols and thiol acetates I [X = HS, MeCOS; R1, R2 = Me2CH, Ph; R32 = (CH2)4, (CH2)5], prepared from the simple natural amino acid (S)-(-)-valine, were found to be effective catalysts for the enantioselective addition of alkenylzinc reagents R4CH:CHZnEt (R4 = n-Bu, Me3C, n-hexyl, Ph) to aldehydes R5CHO (R5 = cyclohexyl, Ph, 2-ClC6H4, 4-MeOC6H4, PhCH:CH) and thereby providing an efficient route to chiral (E)-allylic alcs. II with ees of up to >99%.

IT **160011-80-3P 757243-47-3P 849599-88-8P**
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)
(preparation of β-amino-substituted alcs., thiols and thiol acetates as chiral catalysts for enantioselective alkenylzinc addition to aldehydes)

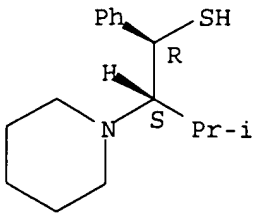
RN 160011-80-3 HCAPLUS
CN 1-Piperidineethanethiol, α,β-diphenyl-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



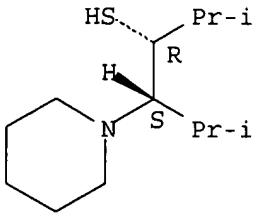
RN 757243-47-3 HCAPLUS
CN 1-Piperidineethanethiol, β-(1-methylethyl)-α-phenyl-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



RN 849599-88-8 HCAPLUS
CN 1-Piperidineethanethiol, α,β-bis(1-methylethyl)-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



REFERENCE COUNT: 28 THERE ARE 28 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L13 ANSWER 3 OF 24 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 2004:759870 HCAPLUS
DOCUMENT NUMBER: 141:277501
TITLE: Preparation of 2-aminoethanethiol compounds as efficient catalysts for asymmetric addition reaction
INVENTOR(S): Yang, Teng-Kuei; Tseng, Shi-Liang; Liu, To; Chen, Nan-Kuang
PATENT ASSIGNEE(S): Taiwan
SOURCE: U.S. Pat. Appl. Publ., 15 pp., Cont.-in-part of U.S. Pat. Appl. 2003 153,781.
CODEN: USXXCO
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 2004181057	A1	20040916	US 2004-807710	20040323
US 20030153781	A1	20030814	US 2002-39557	20020108
US 6861536	B2	20050301		

PRIORITY APPLN. INFO.: US 2002-39557 A2 20020108
OTHER SOURCE(S): MARPAT 141:277501

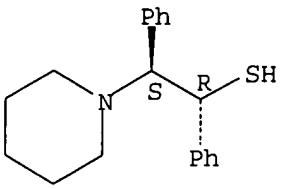
AB The present invention discloses aminothiol compds. having a general formula R3R4NCH(R1)CH(R2)SR5 (wherein R1-R4 = aryl, C1-9 alkyl; or R3, R4 and N form a three- to eight-membered heterocycle; R5 = H, C1-6 alkyl). Such compds. can perform as superior catalysts for the synthesis of chiral secondary alcs. by asym. addition reaction of organic metal compds. such organozinc compound and aldehyde. According to the present invention, the aminothiol compds. are needed only less than 0.02% based on main reactants to obtain enantioselectivity higher than 98% enantiomeric excess, whereby the asym. reactions can become very economic. Thus, cycloalkylation of (2R,3S)-3-amino-4-methylpentan-2-ol by 1,4-dibromobutane in the presence of Na2CO3 in MeCN under refluxing for 12 h gave (2R,3S)-4-methyl-3-(1-pyrrolidinyl)pentan-2-ol which was treated with MeSO2Cl and Et3N in CH2Cl2 for 2 h at 0° for 2 h, concentrated, and reacted with thioacetic acid in benzene at room temperature for 12 h to give 20% (2R,3S)-4-methyl-3-(1-pyrrolidinyl)-2-thioacetylpentane (I) and 40% (3R,4S)-2-methyl-4-(1-pyrrolidinyl)-3-thioacetylpentane (II). I or II was reduced by LiAlH4 in Et2O at 0° for 1 h to give (2R,3S)-4-methyl-3-(1-pyrrolidinyl)pentane-2-thiol or (3R,4S)-2-methyl-4-(1-pyrrolidinyl)pentane-3-thiol (III) in 80% yield. Asym. addition reaction of benzaldehyde with Et2Zn in toluene in the presence of 0.05 mequiv. (equivalence concentration) III at -20° for 12 h gave (R)-2-phenylpropanol (99.6% ee). Chiral

(R)-1-phenyl-2-alken-1-ols were also prepared from butylacetylene and hexylacetylene by monohydroboration of alkynes with BH3.SMe2 and transmetalation of boron to zinc with diethylzinc and asym. addition reaction with benzaldehyde or derivs. using the aminothiol catalysts.

IT **160011-80-3P**, (1R,2S)-1,2-Diphenyl-2-piperidin-1-ylethanethiol
757243-47-3P, (1R,2S)-3-Methyl-1-phenyl-2-piperidin-1-ylbutane-1-thiol
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)
(catalyst; preparation of 2-aminoethanethiol compds. as catalysts for asym. addition reaction of organic metal compound with aldehydes)

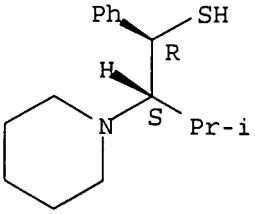
RN 160011-80-3 HCAPLUS
CN 1-Piperidineethanethiol, α,β-diphenyl-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).

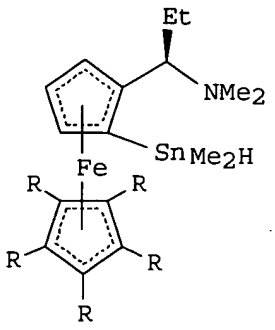


RN 757243-47-3 HCAPLUS
CN 1-Piperidineethanethiol, β-(1-methylethyl)-α-phenyl-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



L13 ANSWER 4 OF 24 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 2003:816945 HCAPLUS
DOCUMENT NUMBER: 140:375280
TITLE: Asymmetric radical reduction with planar chiral organotin hydrides
AUTHOR(S): Kang, Jahyo; Kim, Tae Hyung
CORPORATE SOURCE: Department of Chemistry, Sogang University, Seoul, 121-742, S. Korea
SOURCE: Bulletin of the Korean Chemical Society (2003), 24(8), 1055-1056
CODEN: BKCSDE; ISSN: 0253-2964
PUBLISHER: Korean Chemical Society
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 140:375280
GI



I

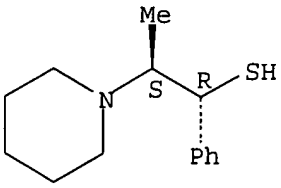
AB It has been shown that the enantioselectivity of hydrogen transfer from the chiral tin hydrides to prochiral radicals is determined by steric interactions between the hydrogen donors and the prochiral radicals. Thus, enantioselective reduction of PhC(Me)(Br)(CO2Me) with tin hydrides I (preparation given; R = H, Me) in THF gave (R)-PhCH(Me)(CO2Me).

IT **166031-49-8**
RL: RGT (Reagent); RACT (Reactant or reagent)
(asym. radical reduction of racemic bromoester with planar chiral ferrocenyl organotin hydrides)

RN 166031-49-8 HCAPLUS

CN 1-Piperidineethanethiol, β-methyl-α-phenyl-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



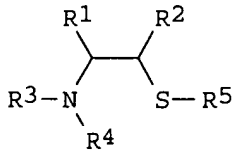
REFERENCE COUNT: 18 THERE ARE 18 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L13 ANSWER 5 OF 24 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 2003:633325 HCAPLUS
DOCUMENT NUMBER: 139:149522
TITLE: Aminothiol compounds and acylated derivatives thereof
INVENTOR(S): Yang, Teng-Kuei; Chen, Nan-Kuang; Liu, To
PATENT ASSIGNEE(S): National Chung-Hsing University, Taiwan
SOURCE: U.S. Pat. Appl. Publ., 5 pp.
CODEN: USXXCO
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

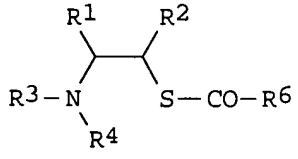
PATENT NO.	KIND	DATE	APPLICATION NO.	DATE

US 2003153781	A1	20030814	US 2002-39557	20020108
US 6861536	B2	20050301		
US 2004049033	A1	20040311	US 2003-650020	20030826
US 6965038	B2	20051115		
US 2004181057	A1	20040916	US 2004-807710	20040323

PRIORITY APPLN. INFO.: US 2002-39557 A3 20020108
OTHER SOURCE(S): MARPAT 139:149522
GI



I



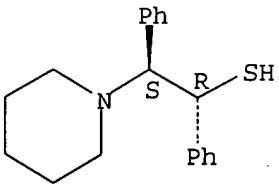
II

AB The present invention discloses aminothiol compds. and acylated derivs. I and II (R1, R2, R3, R4 = C1-9-alkyl or NR3R4 = 3-8-membered heterocycle, R5 and R6 = H, C1-6-alkyl) are substitutable ligands. For example, 1,2-diphenyl-2-pyrrolidinylethanethiol was prepared by the reaction of (1R,2S)-1,2-diphenyl-2-aminoethanol with 1,4-dibromobutane, followed by reaction of MeSO3Cl and reduction by LiAlH4. Such compds. can perform as superior catalysts in asym. addition reactions of organic Zn and aldehyde. According to the present invention, the compds. needed only <0.02% of main reactants to obtain enantioselectivity >99% enantiomeric excess, whereby the asym. reactions can become very economic.

IT **160011-80-3P**
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)
(preparation as asym. addition catalyst with organozinc complexes with aldehydes)

RN 160011-80-3 HCAPLUS
CN 1-Piperidineethanethiol, α,β-diphenyl-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



REFERENCE COUNT: 5 THERE ARE 5 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

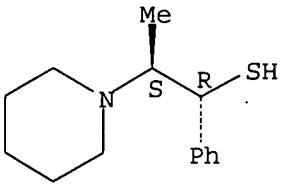
L13 ANSWER 6 OF 24 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 2001:821889 HCAPLUS
DOCUMENT NUMBER: 136:118295
TITLE: Stereoselective synthesis of δ-lactones from 5-oxoalkanals via one-pot sequential acetalization, Tishchenko reaction, and lactonization by cooperative

catalysis of samarium ion and mercaptan
AUTHOR(S): Hsu, Jue-Liang; Fang, Jim-Min
CORPORATE SOURCE: Department of Chemistry, National Taiwan University, Taipei, 106, Taiwan
SOURCE: Journal of Organic Chemistry (2001), 66(25), 8573-8584
CODEN: JOCEAH; ISSN: 0022-3263
PUBLISHER: American Chemical Society
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 136:118295

AB By the synergistic catalysis of samarium ion and mercaptan, a series of 5-oxoalkanals was converted to (substituted) δ-lactones in efficient and stereoselective manners. This one-pot procedure comprises a sequence of acetalization, Tishchenko reaction and lactonization. The deliberative use of mercaptan, by comparison with alc., is advantageous to facilitate the catalytic cycle. The reaction mechanism and stereochem. are proposed and supported by some exptl. evidence. Such samarium ion/mercaptan cocatalyzed reactions show the feature of remote control, which is applicable to the asym. synthesis of optically active δ-lactones. This study also demonstrates the synthesis of two insect pheromones, (2S,5R)-2-methylhexanolide and (R)-hexadecanolide, as examples of a new protocol for asym. reduction of long-chain aliphatic ketones.

IT **166031-49-8P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(one-pot sequential acetalization, Tishchenko reaction, and lactonization by the promotion of samarium ion and mercaptans in stereoselective synthesis of δ-lactones from 5-oxoalkanals)
RN 166031-49-8 HCAPLUS
CN 1-Piperidineethanethiol, β-methyl-α-phenyl-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).

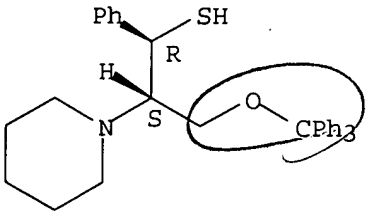


REFERENCE COUNT: 104 THERE ARE 104 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L13 ANSWER 7 OF 24 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 2001:508661 HCAPLUS
DOCUMENT NUMBER: 135:256816
TITLE: A purely synthetic, diversity amenable version of norephedrine thiols for the highly enantioselective diethylzinc addition to aldehydes
AUTHOR(S): Jimeno, Ciril; Moyano, Albert; Pericas, Miquel A.; Riera, Antoni
CORPORATE SOURCE: Unitat Recerca Sintesi Asimetrica, Dep. Quim. Org., Universitat de Barcelona, Barcelona, E-08028, Spain
SOURCE: Synlett (2001), (7), 1155-1157
CODEN: SYNLES; ISSN: 0936-5214
PUBLISHER: Georg Thieme Verlag

DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 135:256816
AB A new β-amino thiol arising from purely synthetic yet enantiopure amino alcs. has been prepared and successfully used in the addition of diethylzinc to aromatic aldehydes, yielding secondary alcs. in ee's up to 99%.
IT **361543-74-0P**
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)
(enantioselective diethylzinc addition to aldehydes catalyzed by β-amino thiols)
RN 361543-74-0 HCAPLUS
CN 1-Piperidineethanethiol, α-phenyl-β-[(triphenylmethoxy)methyl]-, (αR,βS)- (9CI) (CA INDEX NAME)

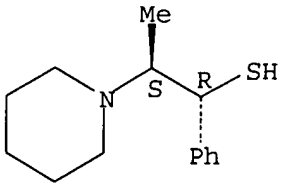
Absolute stereochemistry. Rotation (-).



REFERENCE COUNT: 29 THERE ARE 29 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L13 ANSWER 8 OF 24 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1999:296019 HCAPLUS
DOCUMENT NUMBER: 130:312007
TITLE: A concise synthesis of unnatural (+)-5-epi-nojirimycin-δ-lactam via asymmetric reduction of a meso-imide
AUTHOR(S): Kang, Jahyo; Lee, Choon Woo; Lim, Geun Jho; Cho, Byung Tae
CORPORATE SOURCE: Department of Chemistry, Sogang University, Seoul, 121-742, S. Korea
SOURCE: Tetrahedron: Asymmetry (1999), 10(4), 657-660
CODEN: TASYE3; ISSN: 0957-4166
PUBLISHER: Elsevier Science Ltd.
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 130:312007
AB Nojirimycin-δ-lactam skeleton was synthesized by asym. reduction of a cyclic triacetyloxy meso imide with a chiral β-amino thiol ligand. The resulting product was converted to unnatural (+)-5-epi-nojirimycin-δ-lactam.
IT **166031-49-8**
RL: RCT (Reactant); RACT (Reactant or reagent)
(a concise synthesis of unnatural (+)-epi-nojirimycin-δ-lactam via asym. reduction of a meso-imide)
RN 166031-49-8 HCAPLUS
CN 1-Piperidineethanethiol, β-methyl-α-phenyl-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



REFERENCE COUNT: 18 THERE ARE 18 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

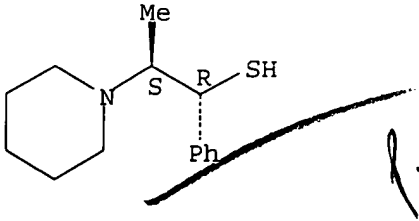
L13 ANSWER 9 OF 24 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1998:801743 HCAPLUS
DOCUMENT NUMBER: 130:153758
TITLE: Asymmetric synthesis of (diene)Fe(CO)3 complexes by a catalytic enantioselective alkylation using dialkylzincs
AUTHOR(S): Takemoto, Yoshiji; Baba, Yasutaka; Honda, Asami; Nakao, Syusuke; Noguchi, Izumi; Iwata, Chuzo; Tanaka, Tetsuaki; Ibuka, Toshiro
CORPORATE SOURCE: Graduate School of Pharmaceutical Sciences, Kyoto University, Kyoto, 606-8501, Japan
SOURCE: Tetrahedron (1998), 54(51), 15567-15580
CODEN: TETRAB; ISSN: 0040-4020
PUBLISHER: Elsevier Science Ltd.
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 130:153758

AB The reaction of meso-(2,4-hexadien-1,6-dial)Fe(CO)3 complex (1) with several alkylzincs in the presence of 50 mol% of (S)-(+)-diphenyl(1-methylpyrrolidin-2-yl)methanol proceeded with high enantiotopic group- and diastereotopic face-selectivity to give (2R,6S)-alc. complexes as major products, except in the case with dimethylzinc (>90% de and >98% ee). On the other hand, the methylation of 1 with Me2Zn proceeded with high enantioselectivity by adding 1.8 equivalent of Ti(Oi-Pr)4 in the presence of 3 mol% of (S,S)-1,2-bis(trifluoromethylsulfonamide)cyclohexane (82% de, 96% ee). The enantioselective alkylation was also applied to the kinetic resolution of racemic (sorbic aldehyde)Fe(CO)3 complex.

IT **166031-49-8**
RL: CAT (Catalyst use); USES (Uses)
(asym. synthesis of diene iron tricarbonyl complexes by catalytic enantioselective alkylation using dialkylzincs)

RN 166031-49-8 HCAPLUS
CN 1-Piperidineethanethiol, β-methyl-α-phenyl-, (αR,βS)- (9CI) (CA INDEX NAME)

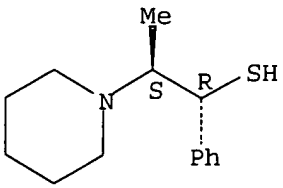
Absolute stereochemistry. Rotation (-).



REFERENCE COUNT: 36 THERE ARE 36 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L13 ANSWER 10 OF 24 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1998:632164 HCAPLUS
DOCUMENT NUMBER: 129:343594
TITLE: Structural chemistry of methyl- and allylpalladium(II) complexes containing chiral thioether auxiliaries
AUTHOR(S): Boog-Wick, Karin; Pregosin, Paul S.; Woerle, Michael; Albinati, Alberto
CORPORATE SOURCE: Lab. Anorganische Chem., ETH Zentrum Zuerich, Zurich, CH-8092, Switz.
SOURCE: Helvetica Chimica Acta (1998), 81(9), 1622-1633
CODEN: HCACAV; ISSN: 0018-019X
PUBLISHER: Verlag Helvetica Chimica Acta AG
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 129:343594
AB The synthesis and mol. structures of two [PdCl(Me)] complexes each containing a different chiral N,S-chelate based on {[(dihydrooxazolyl)phenyl]methyl}thioglucose backbones, i.e., chloro({2-[(4S)-4,5-dihydro-4-isopropyloxazol-2-yl-κN]phenyl}methyl 2,3,4,6-tetra-O-acetyl-1-(thio-κS)-β-D-glucopyranoside)methylpalladium(II) and a [Pd(η3-C3H5)(PS)]+ cation in which the P,S-chelate stems from a phosphinoferrocene and thioephedrine-derived thioether donor as well as [(S)-1-(diphenylphosphino-κP)-2-((1R)-1-{[(1R,2S)-1-phenyl-2-(piperidin-1-yl)propyl]thio-κS}ethyl)ferrocene](η3-prop-2-enyl)palladium trifluoromethanesulfonate are reported. In the methylpalladium compds. the thioglucose-κS moiety is pseudo-axial, whereas in the allyl complex, the thioephedrine-κS moiety is markedly pseudo-equatorial. It is suggested, based on these results, that the shape (chiral pocket) of such coordinated chiral thioethers may not be readily predictable.
IT **166031-49-8**
RL: RCT (Reactant); RACT (Reactant or reagent)
(preparation of methyl- and allylpalladium complexes with chiral thioether moieties)
RN 166031-49-8 HCAPLUS
CN 1-Piperidineethanethiol, β-methyl-α-phenyl-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



L13 ANSWER 11 OF 24 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1998:482774 HCAPLUS
DOCUMENT NUMBER: 129:216335
TITLE: Asymmetric synthesis of a new cylindrically chiral and air-stable ferrocenyldiphosphine and its application to rhodium-catalyzed asymmetric hydrogenation

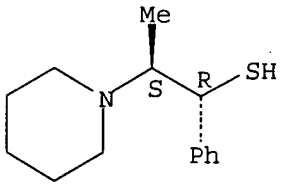
AUTHOR(S): Kang, Jahyo; Lee, Jun Hee; Ahn, Sung Hoon; Choi, Jung Sun
CORPORATE SOURCE: Department of Chemistry and Organic Chemistry Research Center, Sogang University, Seoul, 121-742, S. Korea
SOURCE: Tetrahedron Letters (1998), 39(31), 5523-5526
CODEN: TELEAY; ISSN: 0040-4039
PUBLISHER: Elsevier Science Ltd.
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 129:216335

AB The novel, cylindrically chiral air-stable (S,S)-1,1'-bis(diphenylphosphino)-2,2'-di-3-pentylferrocene [(S,S)-FerroPHOS] ligand was prepared and its in situ rhodium complexes have been applied to asym. hydrogenation. High reactivity and selectivity have been realized in hydrogenation of various dehydroamino acid derivs.

IT **166031-49-8**
RL: RCT (Reactant); RACT (Reactant or reagent)
(asym. synthesis of a new cylindrically chiral and air stable ferrocenyldiphosphine and its application to rhodium catalyzed asym. hydrogenation)

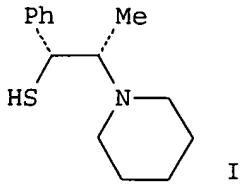
RN 166031-49-8 HCAPLUS
CN 1-Piperidineethanethiol, β-methyl-α-phenyl-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



REFERENCE COUNT: 30 THERE ARE 30 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L13 ANSWER 12 OF 24 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1998:362994 HCAPLUS
DOCUMENT NUMBER: 129:122430
TITLE: Examination of bidentate thiol derivatives as ligands in the Ni-catalyzed asymmetric conjugate addition of diethylzinc to enones
AUTHOR(S): Kang, Jahyo; Kim, Joo In; Lee, Jae Hoon; Kim, Hyo Jung; Byun, Yong Hun
CORPORATE SOURCE: Department of Chemistry, Sogang University, Seoul, 121-742, S. Korea
SOURCE: Bulletin of the Korean Chemical Society (1998), 19(5), 601-603
CODEN: BKCSDE; ISSN: 0253-2964
PUBLISHER: Korean Chemical Society
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 129:122430
GI



I

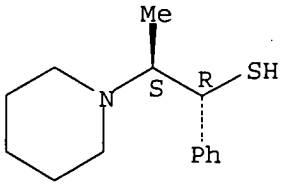
AB Asym. conjugate addition of diethylzinc to (E)-PhCH:CHCOPh was catalyzed by Ni(II) complexes, e.g. Ni(acac)2 or NiCl2, in presence of bidentate thiol ligands, e.g. I. The major enantiomer obtained was (R)-PhCHEtCH2COPh.

IT **166031-49-8**
RL: CAT (Catalyst use); USES (Uses)
(asym. conjugate addition of diethylzinc to enones catalyzed by Ni(II) and bidentate thiol ligands)

RN 166031-49-8 HCAPLUS

CN 1-Piperidineethanethiol, β-methyl-α-phenyl-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



REFERENCE COUNT: 51 THERE ARE 51 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L13 ANSWER 13 OF 24 HCAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 1998:272187 HCAPLUS

DOCUMENT NUMBER: 129:54427

TITLE: The interaction of chiral amino thiols with organozinc reagents and aldehydes: a mechanism of amino thiol-catalyzed addition of organozinc reagents to aldehydes

AUTHOR(S): Kang, Jahyo; Kim, Jin Bum; Kim, Jeeyoung; Lee, Duckhwan

CORPORATE SOURCE: Department of Chemistry, Sogang University, Seoul, 121-742, S. Korea

SOURCE: Bulletin of the Korean Chemical Society (1998), 19(4), 475-481
CODEN: BKCSDE; ISSN: 0253-2964

PUBLISHER: Korean Chemical Society

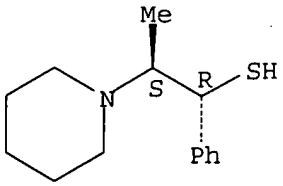
DOCUMENT TYPE: Journal

LANGUAGE: English

AB Details of various equilibrium involved in the reactions of oxaza- and thiazazincolidine catalysts, generated from either β-amino alc. or β-amino thiol, with benzaldehyde were studied by colligative measurements. The coordination of diethylzinc prior to the coordination of aldehyde is essential for high enantioselectivity of the thiol catalyzed reaction. The probable origin of asym. nonlinearity is also presented.

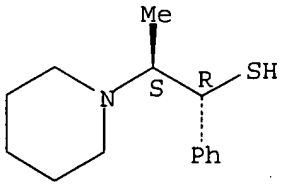
IT **166031-49-8 188711-05-9**
RL: RCT (Reactant); RACT (Reactant or reagent)
(mechanism of amino thiol-catalyzed addition of organozinc reagents to aldehydes)
RN 166031-49-8 HCAPLUS
CN 1-Piperidineethanethiol, β-methyl-α-phenyl-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



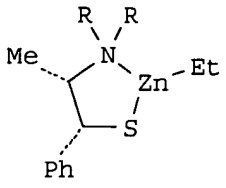
RN 188711-05-9 HCAPLUS
CN 1-Piperidineethanethiol, β-methyl-α-phenyl-, (αR,βS)-rel- (9CI) (CA INDEX NAME)

Relative stereochemistry.

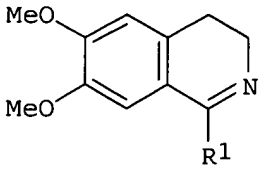


REFERENCE COUNT: 14 THERE ARE 14 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

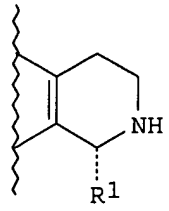
L13 ANSWER 14 OF 24 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1997:213617 HCAPLUS
DOCUMENT NUMBER: 126:277632
TITLE: Enantioselective catalytic reduction of dihydroisoquinoline derivatives
AUTHOR(S): Kang, Jahyo; Kim, Jin Bum; Cho, Kwi Hyung; Cho, Byung Tae
CORPORATE SOURCE: Department of Chemistry, Sogang University, Seoul, 121-742, S. Korea
SOURCE: Tetrahedron: Asymmetry (1997), 8(5), 657-660
CODEN: TASYE3; ISSN: 0957-4166
PUBLISHER: Elsevier
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 126:277632
GI



I



II



III

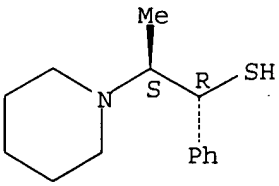
AB Zinc complexes I [RR = (CH2)5, R = Me] were shown to be excellent catalysts for enantioselective reduction of dihydroisoquinolines II (R1 = Me, 3,4-dimethoxy-, 3,4,5-trimethoxybenzyl, 3,4-dimethoxyphenyl) with BH3·THF to the corresponding (R)-tetrahydroisoquinolines III with good enantioselectivity.

IT **166031-49-8**
RL: RCT (Reactant); RACT (Reactant or reagent)
(enantioselective catalytic reduction of dihydroisoquinoline derivs.)

RN 166031-49-8 HCAPLUS

CN 1-Piperidineethanethiol, β-methyl-α-phenyl-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



REFERENCE COUNT: 47 THERE ARE 47 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L13 ANSWER 15 OF 24 HCAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 1997:133573 HCAPLUS

DOCUMENT NUMBER: 126:263720

TITLE: The effects of sulfur substitution in chiral amino thiols on the enantioselective addition of organozinc reagents to aldehydes: a novel method for estimation of free energies of dimerization in monomer-dimer equilibria

AUTHOR(S): Kang, Jahyo; Kim, Jin Bum; Kim, Jeong Whan; Lee, Duckhwan

CORPORATE SOURCE: Dep. of Chemistry, Sogang University, Seoul, 121-742, S. Korea

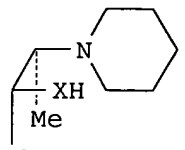
SOURCE: Journal of the Chemical Society, Perkin Transactions 2: Physical Organic Chemistry (1997), (2), 189-194
CODEN: JCPKBH; ISSN: 0300-9580

PUBLISHER: Royal Society of Chemistry

DOCUMENT TYPE: Journal

LANGUAGE: English

GI



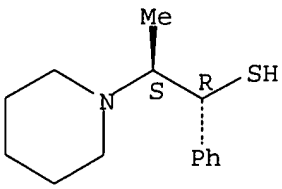
I

AB Differences between the thiol ligand I (X = S) and the corresponding alc. ligand (X = O) were observed in the catalytic asym. alkylation of benzaldehyde with diethylzinc. The thiol ligand was superior for reaction rate, enantioselectivity and asym. amplification. The effects of chiral amino thiols are discussed and compared with the results of chiral amino alc. counterparts. The quant. and thermodn. aspects of the monomer-dimer equilibrium involved in thiazazincolidine or oxazazincolidine catalysts have also been studied on the basis of colligative properties.

IT **166031-49-8 188711-05-9 188711-34-4**
RL: CAT (Catalyst use); PEP (Physical, engineering or chemical process); PRP (Properties); RCT (Reactant); PROC (Process); RACT (Reactant or reagent); USES (Uses)
(effect of sulfur substitution in chiral amino thiols on enantioselective addition of organozinc reagents to aldehydes, and colligative estimation of free energies of dimerization in monomer-dimer equilibrium)

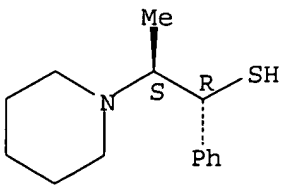
RN 166031-49-8 HCAPLUS
CN 1-Piperidineethanethiol, β-methyl-α-phenyl-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



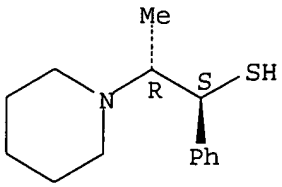
RN 188711-05-9 HCAPLUS
CN 1-Piperidineethanethiol, β-methyl-α-phenyl-, (αR,βS)-rel- (9CI) (CA INDEX NAME)

Relative stereochemistry.



RN 188711-34-4 HCAPLUS
CN 1-Piperidineethanethiol, β-methyl-α-phenyl-, [S-(R*,S*)]- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



REFERENCE COUNT: 16 THERE ARE 16 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

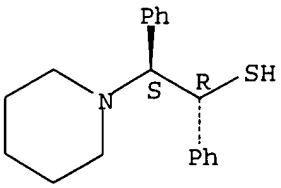
L13 ANSWER 16 OF 24 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1997:39785 HCAPLUS
DOCUMENT NUMBER: 126:131036
TITLE: Chiral β-amino thiol catalysts for the enantioselective addition of diethylzinc to aldehydes
AUTHOR(S): Kang, Jahyo; Kim, Jeong Whan; Lee, Jun Won; Kim, Dong Soo; Kim, Joo In
CORPORATE SOURCE: Dep. Chem., Sogang Univ., Seoul, 121-742, S. Korea
SOURCE: Bulletin of the Korean Chemical Society (1996), 17(12), 1135-1142
CODEN: BKCSDE; ISSN: 0253-2964
PUBLISHER: Korean Chemical Society
DOCUMENT TYPE: Journal
LANGUAGE: English

AB Reaction of diethylzinc with α-branched aldehydes in the presence of a catalytic amount (5 mol %) of various β-amino thiols in toluene or ether provided the corresponding secondary alcs. in outstanding ee. Detailed preparative procedure for the β-amino thiols are presented.

IT **160011-80-3P**
RL: CAT (Catalyst use); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent); USES (Uses)
(enantioselective addition of diethylzinc to aldehydes using chiral β-amino thiol catalysts)

RN 160011-80-3 HCAPLUS
CN 1-Piperidineethanethiol, α,β-diphenyl-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).

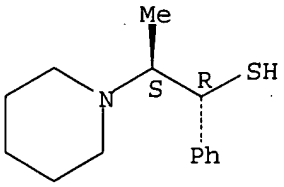


IT **166031-49-8P 186314-16-9P**
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)
(enantioselective addition of diethylzinc to aldehydes using chiral β-amino thiol catalysts)

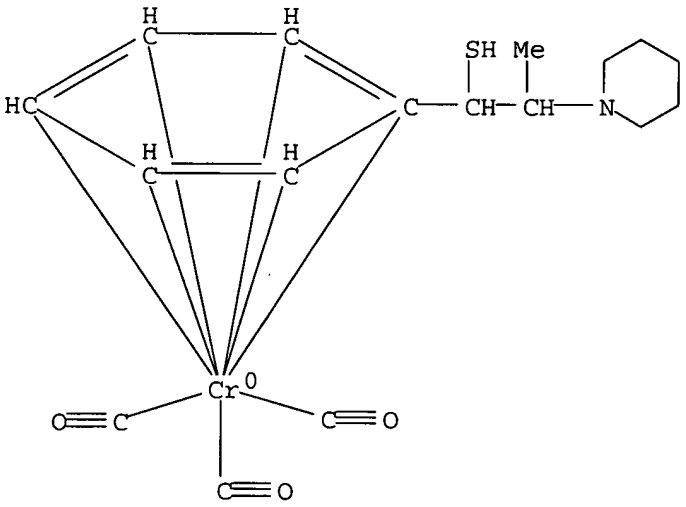
RN 166031-49-8 HCAPLUS

CN 1-Piperidineethanethiol, β-methyl-α-phenyl-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).

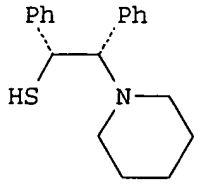


RN 186314-16-9 HCAPLUS
CN Chromium, tricarbonyl[β-methyl-α-(η6-phenyl)-1-piperidineethanethiol]-, stereoisomer (9CI) (CA INDEX NAME)

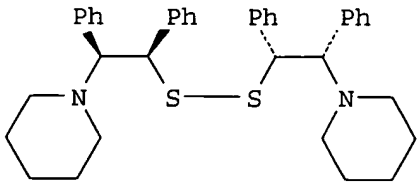


REFERENCE COUNT: 29 THERE ARE 29 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L13 ANSWER 17 OF 24 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1995:194984 HCAPLUS
DOCUMENT NUMBER: 122:55341
TITLE: Enantioselective addition of diethylzinc to aldehydes catalyzed by a drug-unrelated chiral amino thiol and the corresponding disulfide
AUTHOR(S): Kang, Jahyo; Kim, Dong Soo; Kim, Joo In
CORPORATE SOURCE: Department Chemistry, Sogang University, Seoul, 121-742, S. Korea
SOURCE: Synlett (1994), (10), 842-4
CODEN: SYNLES; ISSN: 0936-5214
PUBLISHER: Thieme
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 122:55341
GI



I



II

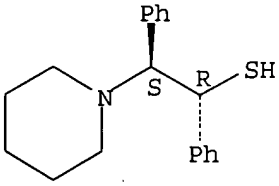
AB Reaction of diethylzinc with aldehydes in the presence of a catalytic amount of a β-amino thiol I (5 mol %) and the disulfide II (2.5 mol %) in toluene at 0° provided the corresponding secondary alcs. in excellent ee's.

IT **160011-80-3P**
RL: CAT (Catalyst use); RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent); USES (Uses)
(enantioselective addition of diethylzinc with aldehydes catalyzed by chiral amino thiol and disulfide)

RN 160011-80-3 HCAPLUS

CN 1-Piperidineethanethiol, α,β-diphenyl-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



L13 ANSWER 18 OF 24 HCAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 1995:86424 HCAPLUS

DOCUMENT NUMBER: 123:142957

TITLE: Enantioselective addition of diethylzinc to α-branched aldehydes

AUTHOR(S): Kang, Jahyo; Lee, Jun Won; Kim, Joo In

CORPORATE SOURCE: Department of Chemistry, Sogang University, Seoul, 121-742, S. Korea

SOURCE: Journal of the Chemical Society, Chemical Communications (1994), (17), 2009-10
CODEN: JCCCAT; ISSN: 0022-4936

DOCUMENT TYPE: Journal

LANGUAGE: English

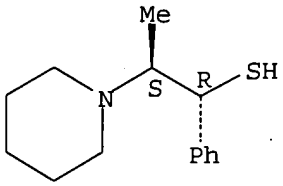
OTHER SOURCE(S): CASREACT 123:142957

AB Reaction of diethylzinc with α-branched aldehydes in the presence of a catalytic amount of (1R,2S)-(-)-1-phenyl-2-piperidinopropane-1-thiol provided the corresponding secondary alcs. in almost 100% enantiomeric excess.

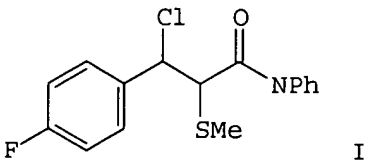
IT **166031-49-8P**
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)
(best catalyst; as ligand catalyst for enantioselective addition of diethylzinc to α-branched aldehydes)

RN 166031-49-8 HCAPLUS
CN 1-Piperidineethanethiol, β-methyl-α-phenyl-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



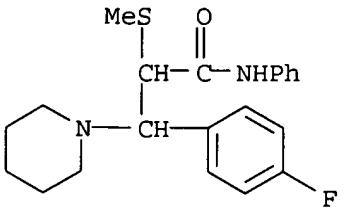
L13 ANSWER 19 OF 24 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1994:604916 HCAPLUS
DOCUMENT NUMBER: 121:204916
TITLE: Synthesis and biological activity of 3-chloro(or piperidyl)-3-(p-fluorophenyl)-2-(methylthio)propanamides
AUTHOR(S): Vidugiriene, V.; Valaviciene, J.; Stumbreviciute, Z.; Karpavicius, K.
CORPORATE SOURCE: Inst. Biochemistry, Vilnius, Lithuania
SOURCE: Chemija (1993), (4), 50-4
CODEN: CHMJES; ISSN: 0235-7216
DOCUMENT TYPE: Journal
LANGUAGE: English
GI



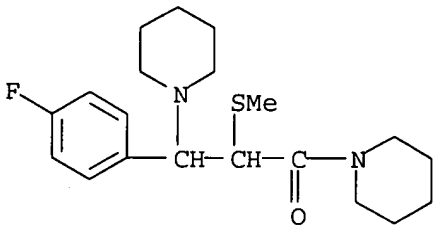
I

AB Treatment of 3-(p-fluorophenyl)propenamide with methylsulfenylchloride gave erythro-3-chloro-3-(p-fluorophenyl)-2-(methylthio)-N-phenylpropanamide (I). The elimination of HCl or the substitution of Cl with piperidine in the above-mentioned compds. led to substituted propenamides and propenoic acids. The toxicity and antitumor activity of these compds. were studied.

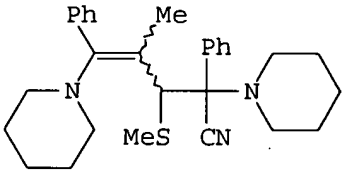
IT **157946-55-9P 157946-56-0P**
RL: BAC (Biological activity or effector, except adverse); BSU (Biological study, unclassified); SPN (Synthetic preparation); THU (Therapeutic use); BIOL (Biological study); PREP (Preparation); USES (Uses)
(preparation of, as neoplasm inhibitor)
RN 157946-55-9 HCAPLUS
CN 1-Piperidinepropanamide, β-(4-fluorophenyl)-α-(methylthio)-N-phenyl- (9CI) (CA INDEX NAME)



RN 157946-56-0 HCAPLUS
CN Piperidine, 1-[3-(4-fluorophenyl)-2-(methylthio)-1-oxo-3-(1-piperidinyl)propyl]- (9CI) (CA INDEX NAME)



L13 ANSWER 20 OF 24 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1993:560233 HCAPLUS
DOCUMENT NUMBER: 119:160233
TITLE: Reactions of carbanions generated from 2-(dialkylamino)-2-phenylacetonitriles with disubstituted acetylenes
AUTHOR(S): Zdrojewski, Tadeusz; Jonczyk, Andrzej
CORPORATE SOURCE: Dep. Chem., Tech. Univ. (Politechnika), Warsaw, 00-662, Pol.
SOURCE: Liebigs Annalen der Chemie (1993), (4), 375-8
CODEN: LACHDL; ISSN: 0170-2041
DOCUMENT TYPE: Journal
LANGUAGE: English
GI



II

AB Reactions of aminonitriles PhCH(NR12)CN [R12 = (CH2)5, (CH2)4, (CH2)2O(CH2)2, (CH2)2S(CH2)2, (CH2)2NMe(CH2)2] with MeC.tplbond.CR2 (R2 = SMe, Ph), carried out in DMSO in the presence of powdered sodium hydroxide and benzyltriethylammonium chloride (TEBAC) as a catalyst, afford either PhC(NR12)(CN)CMe:CHR2 (I) as the E/Z isomer mixture or the pure E isomer or a mixture of I (R2 = SMe) and dipiperidinopentenenitrile II; unmasking of the carbonyl group in I [R12 = (CH2)5, R2 = Ph] and II gives ketones

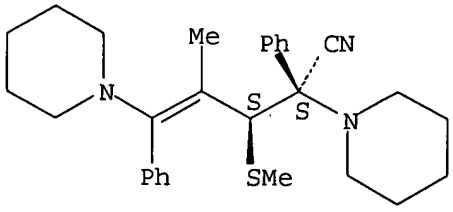
PhCOCMe:CHPh and PhCOCHMeCH(SMe)COPh, resp.

IT **150179-13-8P 150179-14-9P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation and cleavage of)

RN 150179-13-8 HCAPLUS

CN 1-Piperidineacetonitrile, α-[2-methyl-1-(methylthio)-3-phenyl-3-(1-piperidinyl)-2-propenyl]-α-phenyl-, (R*,R*)- (9CI) (CA INDEX NAME)

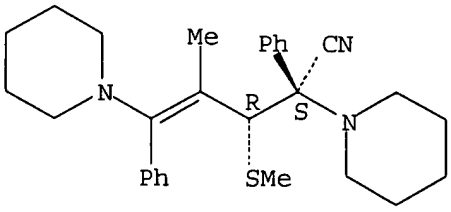
Relative stereochemistry.
Double bond geometry unknown.



RN 150179-14-9 HCAPLUS

CN 1-Piperidineacetonitrile, α-[2-methyl-1-(methylthio)-3-phenyl-3-(1-piperidinyl)-2-propenyl]-α-phenyl-, (R*,S*)- (9CI) (CA INDEX NAME)

Relative stereochemistry.
Double bond geometry unknown.



L13 ANSWER 21 OF 24 HCAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 1991:228476 HCAPLUS

DOCUMENT NUMBER: 114:228476

TITLE: Synthesis and study of derivatives of 3-(alkylamino)-2-(methylthio)carboxylic acids

AUTHOR(S): Vidugiriene, V.; Valaviciene, J.; Rasteikiene, L.

CORPORATE SOURCE: Inst. Biokhim., Vilnius, USSR

SOURCE: Chemija (1990), (2), 101-6
CODEN: CHMJES; ISSN: 0235-7216

DOCUMENT TYPE: Journal

LANGUAGE: Russian

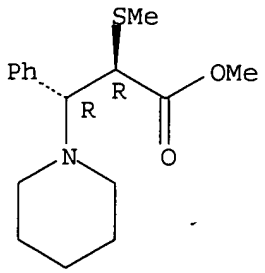
OTHER SOURCE(S): CASREACT 114:228476

AB Treating Z-RCH:C(SMe)COX (R = Ph, Me, X = NHPh; R = Ph, X = OMe) and RCHClCH(SMe)COX (same R, X) with 2-4 equiv HA (A = piperidino, morpholino, cyclohexylamino, ethylenimino, NHC5H11-n) gave 10 corresponding RCHACH(SMe)COX (I) as erythro-threo mixts. I had low-to-moderate toxicity and antitumor activity, with I (R = Ph, A = piperidino, X = NHPh) showing the best profile.

IT **133508-72-2P 133508-73-3P 133508-80-2P**
133508-81-3P 133612-17-6P 133612-23-4P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation, toxicity, and antineoplastic activity of)

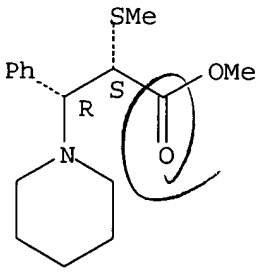
RN 133508-72-2 HCAPLUS
CN 1-Piperidinepropanoic acid, α-(methylthio)-β-phenyl-, methyl ester, (R*,R*)- (9CI) (CA INDEX NAME)

Relative stereochemistry.



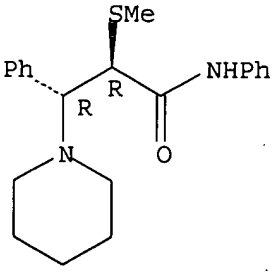
RN 133508-73-3 HCAPLUS
CN 1-Piperidinepropanoic acid, α-(methylthio)-β-phenyl-, methyl ester, (R*,S*)- (9CI) (CA INDEX NAME)

Relative stereochemistry.



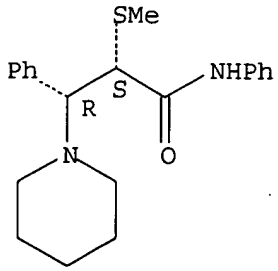
RN 133508-80-2 HCAPLUS
CN 1-Piperidinepropanamide, α-(methylthio)-N,β-diphenyl-, (R*,R*)- (9CI) (CA INDEX NAME)

Relative stereochemistry.



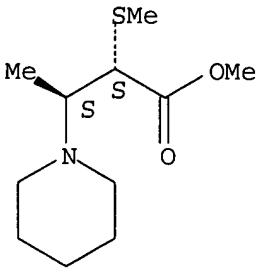
RN 133508-81-3 HCAPLUS
CN 1-Piperidinepropanamide, α-(methylthio)-N,β-diphenyl-, (R*,S*)- (9CI) (CA INDEX NAME)

Relative stereochemistry.



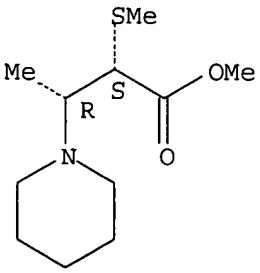
RN 133612-17-6 HCAPLUS
CN 1-Piperidinepropanoic acid, β-methyl-α-(methylthio)-, methyl ester, (R*,R*)- (9CI) (CA INDEX NAME)

Relative stereochemistry.



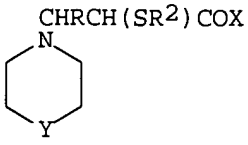
RN 133612-23-4 HCAPLUS
CN 1-Piperidinepropanoic acid, β-methyl-α-(methylthio)-, methyl ester, (R*,S*)- (9CI) (CA INDEX NAME)

Relative stereochemistry.



L13 ANSWER 22 OF 24 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1991:206268 HCAPLUS
DOCUMENT NUMBER: 114:206268
TITLE: Nucleophilic addition of amines to derivatives of unsaturated acids containing 2-alkyl(phenyl)thio groups
AUTHOR(S): Talaikyte, Z.; Vidugiriene, V.; Rasteikiene, L.
CORPORATE SOURCE: Inst. Biokhim., Vilnius, USSR
SOURCE: Chemija (1990), (2), 93-100

CODEN: CHMJES; ISSN: 0235-7216
DOCUMENT TYPE: Journal
LANGUAGE: Russian
GI



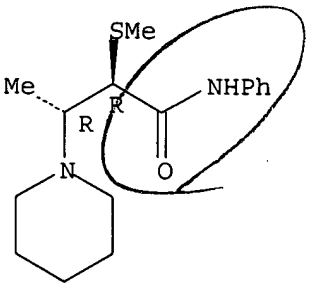
I

AB The title reaction of piperidine or morpholine with RCH:C(SR1)COX (R = Me, Ph; R1 = Me, Ph, CH2CH2Cl; X = NHPh, OMe) is nonstereospecific and gives mixts. of derivs. of erythro- and threo-butanoic acid I (R = Me, R2 = Me, piperidino- or morpholinoethyl; Y = CH2, O) or -phenylpropanoic acid I (R = Ph).

IT **133508-66-4P 133508-67-5P 133508-72-2P**
133508-73-3P 133508-80-2P 133508-81-3P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of)

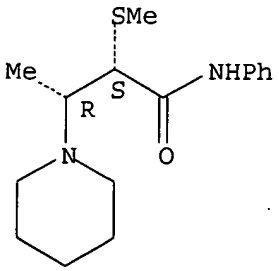
RN 133508-66-4 HCAPLUS
CN 1-Piperidinepropanamide, β-methyl-α-(methylthio)-N-phenyl-, (R*,R*)- (9CI) (CA INDEX NAME)

Relative stereochemistry.



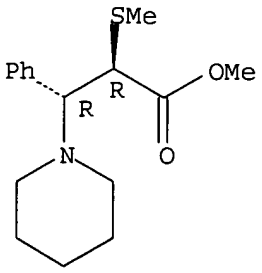
RN 133508-67-5 HCAPLUS
CN 1-Piperidinepropanamide, β-methyl-α-(methylthio)-N-phenyl-, (R*,S*)- (9CI) (CA INDEX NAME)

Relative stereochemistry.



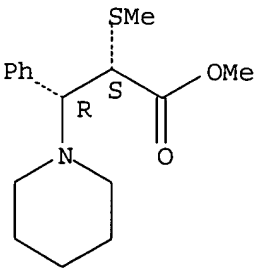
RN 133508-72-2 HCAPLUS
CN 1-Piperidinepropanoic acid, α-(methylthio)-β-phenyl-, methyl ester, (R*,R*)- (9CI) (CA INDEX NAME)

Relative stereochemistry.



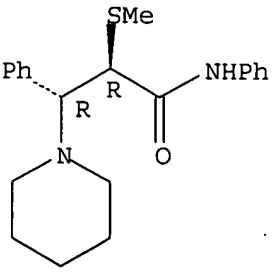
RN 133508-73-3 HCAPLUS
CN 1-Piperidinepropanoic acid, α-(methylthio)-β-phenyl-, methyl ester, (R*,S*)- (9CI) (CA INDEX NAME)

Relative stereochemistry.



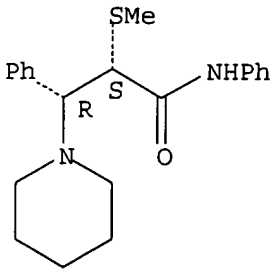
RN 133508-80-2 HCAPLUS
CN 1-Piperidinepropanamide, α-(methylthio)-N,β-diphenyl-, (R*,R*)- (9CI) (CA INDEX NAME)

Relative stereochemistry.



RN 133508-81-3 HCAPLUS
CN 1-Piperidinepropanamide, α-(methylthio)-N,β-diphenyl-, (R*,S*)- (9CI) (CA INDEX NAME)

Relative stereochemistry.

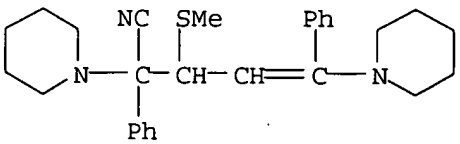


L13 ANSWER 23 OF 24 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1990:458617 HCAPLUS
DOCUMENT NUMBER: 113:58617
TITLE: Reactions of organic anions. 168. Reactions of 2-(dialkylamino)arylacetonitriles with acetylenes under basic conditions. A simple synthesis of substituted mono- and diketones
AUTHOR(S): Zdrojewski, T.; Jonczyk, A.
CORPORATE SOURCE: Dep. Chem., Tech. Univ., Warsaw, PL-00-662, Pol.
SOURCE: Synthesis (1990), (3), 224-33
CODEN: SYNTBF; ISSN: 0039-7881
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 113:58617

AB The reaction of RCH(CN)NR12 (I; R = Ph, 4-MeC6H4, 4-MeOC6H4; R1 = Me; NR12 = piperidino, morpholino, etc.) with R2C.tplbond.CH (II; R2 = Ph, MeS) gave R12NCR(CN)CH:CHR2 (III) and/or R12NCR(CN)CHR2CH:CRNR12; the product depended on the basicity of the amino group in III. I also added to C-1 of II (R2 = EtO) to give R12NCR(CN)C(OEt):CH2. All these products could be hydrolyzed to give mono- or diketones.

IT **128407-40-9P**
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and hydrolysis of)

RN 128407-40-9 HCAPLUS
CN 1-Piperidineacetonitrile, α-[1-(methylthio)-3-phenyl-3-(1-piperidinyl)-2-propenyl]-α-phenyl- (9CI) (CA INDEX NAME)



L13 ANSWER 24 OF 24 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1964:447807 HCAPLUS
DOCUMENT NUMBER: 61:47807
ORIGINAL REFERENCE NO.: 61:8284a-b
TITLE: Preparation of quaternary ammonium betaine salts
INVENTOR(S): Klass, Donald L.
PATENT ASSIGNEE(S): Pure Oil Co.
SOURCE: 4 pp.

DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 3131189		19640428	US 1961-145464	19611016
PRIORITY APPLN. INFO.:			US	19611016

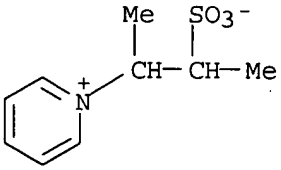
GI For diagram(s), see printed CA Issue.

AB Carbyl sulfate (I), prepared by the reaction of 2 moles SO3 and 1 mole ethylene, reacted with a tertiary amine to form betaines. Thus 1.5 g. pyridine (II) in 10 ml. ethylene dichloride was added to 3 g. I in 30 ml. ethylene dichloride (the reaction was exothermic), the liquid decanted from the precipitate, and the precipitate covered with petr. ether and cooled to give IIa (R = R1 = H), m. 250-5° (HCONMe2). I was also treated with the following to form betaines: quinoline, acridine, trimethylamine, and dimethylaniline (III). Also reported without details were: IIa (R = Ph, R1 = H); Et3NCHEtCH2SO3; IIa (R = R1 = Me); and PhNMe2CMe2CMe2SO3. These compds. are useful intermediates for the preparation of detergents. (Cf. U.S. 2,666,788, or Brit. 686,061.)

IT **859804-42-5**, Pyridinium, 1-(1-methyl-2-sulfopropyl)-, hydroxide, inner salt
(preparation of)

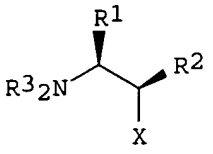
RN 859804-42-5 HCAPLUS

CN Pyridinium, 1-(1-methyl-2-sulfopropyl)-, hydroxide, inner salt (7CI) (CA INDEX NAME)

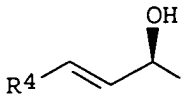


=> d l14 ibib abs hitstr tot

L14 ANSWER 1 OF 9 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 2005:130245 HCAPLUS
DOCUMENT NUMBER: 142:373291
TITLE: New β-amino thiols as efficient catalysts for highly enantioselective alkenylzinc addition to aldehydes
AUTHOR(S): Tseng, Shi-Liang; Yang, Teng-Kuei
CORPORATE SOURCE: Department of Chemistry, National Chung-Hsing University, Taichung, 40227, Peop. Rep. China
SOURCE: Tetrahedron: Asymmetry (2005), 16(4), 773-782
CODEN: TASYE3; ISSN: 0957-4166
PUBLISHER: Elsevier B.V.
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 142:373291
GI



I



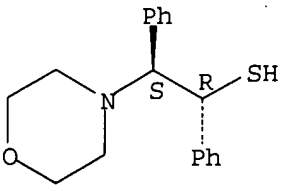
II

AB A series of new optically active β-amino thiols and thiol acetates I [X = HS, MeCOS; R1, R2 = Me2CH, Ph; R32 = (CH2)4, (CH2)5], prepared from the simple natural amino acid (S)-(-)-valine, were found to be effective catalysts for the enantioselective addition of alkenylzinc reagents R4CH:CHZnEt (R4 = n-Bu, Me3C, n-hexyl, Ph) to aldehydes R5CHO (R5 = cyclohexyl, Ph, 2-ClC6H4, 4-MeOC6H4, PhCH:CH) and thereby providing an efficient route to chiral (E)-allylic alcs. II with ees of up to >99%.

IT **757243-55-3P 849599-91-3P 849599-94-6P**
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)
(preparation of β-amino-substituted alcs., thiols and thiol acetates as chiral catalysts for enantioselective alkenylzinc addition to aldehydes)

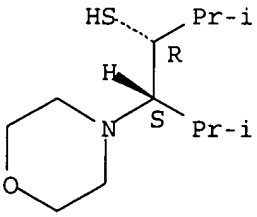
RN 757243-55-3 HCAPLUS
CN 4-Morpholineethanethiol, α,β-diphenyl-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



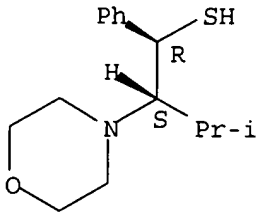
RN 849599-91-3 HCAPLUS
CN 4-Morpholineethanethiol, α,β-bis(1-methylethyl)-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



RN 849599-94-6 HCAPLUS
CN 4-Morpholineethanethiol, β-(1-methylethyl)-α-phenyl-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



REFERENCE COUNT: 28 THERE ARE 28 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L14 ANSWER 2 OF 9 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 2004:759870 HCAPLUS
DOCUMENT NUMBER: 141:277501
TITLE: Preparation of 2-aminoethanethiol compounds as efficient catalysts for asymmetric addition reaction
INVENTOR(S): Yang, Teng-Kuei; Tseng, Shi-Liang; Liu, To; Chen, Nan-Kuang
PATENT ASSIGNEE(S): Taiwan
SOURCE: U.S. Pat. Appl. Publ., 15 pp., Cont.-in-part of U.S. Pat. Appl. 2003 153,781.
CODEN: USXXCO
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 2004181057	A1	20040916	US 2004-807710	20040323
US 2003153781	A1	20030814	US 2002-39557	20020108
US 6861536	B2	20050301		

PRIORITY APPLN. INFO.: US 2002-39557 A2 20020108
OTHER SOURCE(S): MARPAT 141:277501

AB The present invention discloses aminothiol compds. having a general formula R3R4NCH(R1)CH(R2)SR5 (wherein R1-R4 = aryl, C1-9 alkyl; or R3, R4 and N form a three- to eight-membered heterocycle; R5 = H, C1-6 alkyl). Such compds. can perform as superior catalysts for the synthesis of chiral secondary alcs. by asym. addition reaction of organic metal compds. such organozinc compound and aldehyde. According to the present invention, the aminothiol compds. are needed only less than 0.02% based on main reactants to obtain enantioselectivity higher than 98% enantiomeric excess, whereby the asym. reactions can become very economic. Thus, cycloalkylation of (2R,3S)-3-amino-4-methylpentan-2-ol by 1,4-dibromobutane in the presence of Na2CO3 in MeCN under refluxing for 12 h gave (2R,3S)-4-methyl-3-(1-pyrrolidinyl)pentan-2-ol which was treated with MeSO2Cl and Et3N in CH2Cl2 for 2 h at 0° for 2 h, concentrated, and reacted with thioacetic acid in benzene at room temperature for 12 h to give 20% (2R,3S)-4-methyl-3-(1-pyrrolidinyl)-2-thioacetylpentane (I) and 40% (3R,4S)-2-methyl-4-(1-pyrrolidinyl)-3-thioacetylpentane (II). I or II was reduced by LiAlH4 in Et2O at 0° for 1 h to give (2R,3S)-4-methyl-3-(1-pyrrolidinyl)pentane-2-thiol or (3R,4S)-2-methyl-4-(1-pyrrolidinyl)pentane-3-thiol (III) in 80% yield. Asym. addition reaction of benzaldehyde with Et2Zn in toluene in the presence of 0.05 mequiv. (equivalence concentration) III at -20° for 12 h gave (R)-2-phenylpropanol (99.6% ee). Chiral

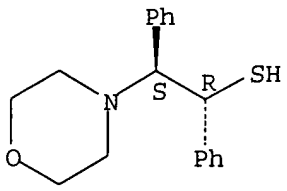
(R)-1-phenyl-2-alken-1-ols were also prepared from butylacetylene and hexylacetylene by monohydroboration of alkynes with BH3.SMe2 and transmetalation of boron to zinc with diethylzinc and asym. addition reaction with benzaldehyde or derivs. using the aminothiol catalysts.

IT **757243-55-3P**, (1R,2S)-1,2-Diphenyl-2-morpholin-4-ylethane-1-thiol
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)
(catalyst; preparation of 2-aminoethanethiol compds. as catalysts for asym. addition reaction of organic metal compound with aldehydes)

RN 757243-55-3 HCAPLUS

CN 4-Morpholineethanethiol, α,β-diphenyl-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



L14 ANSWER 3 OF 9 HCAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 1991:228476 HCAPLUS

DOCUMENT NUMBER: 114:228476

TITLE: Synthesis and study of derivatives of 3-(alkylamino)-2-(methylthio)carboxylic acids

AUTHOR(S): Vidugiriene, V.; Valaviciene, J.; Rasteikiene, L.

CORPORATE SOURCE: Inst. Biokhim., Vilnius, USSR

SOURCE: Chemija (1990), (2), 101-6
CODEN: CHMJES; ISSN: 0235-7216

DOCUMENT TYPE: Journal

LANGUAGE: Russian

OTHER SOURCE(S): CASREACT 114:228476

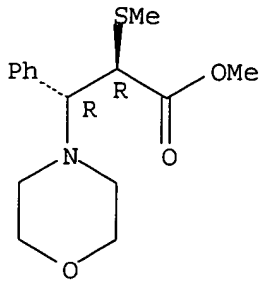
AB Treating Z-RCH:C(SMe)COX (R = Ph, Me, X = NHPh; R = Ph, X = OMe) and RCHClCH(SMe)COX (same R, X) with 2-4 equiv HA (A = piperidino, morpholino, cyclohexylamino, ethylenimino, NHC5H11-n) gave 10 corresponding RCHACH(SMe)COX (I) as erythro-threo mixts. I had low-to-moderate toxicity and antitumor activity, with I (R = Ph, A = piperidino, X = NHPh) showing the best profile.

IT **133508-74-4P 133508-75-5P 133508-82-4P 133508-83-5P 133612-15-4P 133612-21-2P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation, toxicity, and antineoplastic activity of)

RN 133508-74-4 HCAPLUS

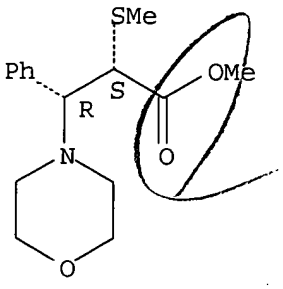
CN 4-Morpholinepropanoic acid, α-(methylthio)-β-phenyl-, methyl ester, (R*,R*)- (9CI) (CA INDEX NAME)

Relative stereochemistry.



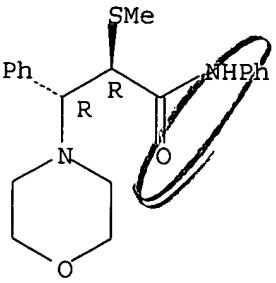
RN 133508-75-5 HCAPLUS
CN 4-Morpholinepropanoic acid, α-(methylthio)-β-phenyl-, methyl ester, (R*,S*)- (9CI) (CA INDEX NAME)

Relative stereochemistry.



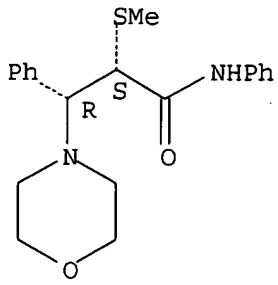
RN 133508-82-4 HCAPLUS
CN 4-Morpholinepropanamide, α-(methylthio)-N,β-diphenyl-, (R*,R*)- (9CI) (CA INDEX NAME)

Relative stereochemistry.



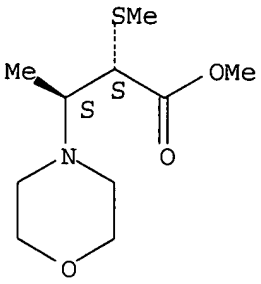
RN 133508-83-5 HCAPLUS
CN 4-Morpholinepropanamide, α-(methylthio)-N,β-diphenyl-, (R*,S*)- (9CI) (CA INDEX NAME)

Relative stereochemistry.



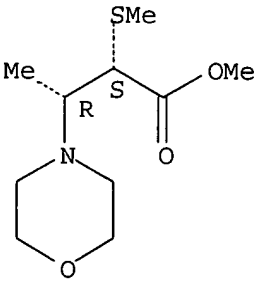
RN 133612-15-4 HCAPLUS
CN 4-Morpholinepropanoic acid, β-methyl-α-(methylthio)-, methyl ester, (R*,R*)- (9CI) (CA INDEX NAME)

Relative stereochemistry.



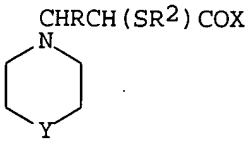
RN 133612-21-2 HCAPLUS
CN 4-Morpholinepropanoic acid, β-methyl-α-(methylthio)-, methyl ester, (R*,S*)- (9CI) (CA INDEX NAME)

Relative stereochemistry.



L14 ANSWER 4 OF 9 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1991:206268 HCAPLUS
DOCUMENT NUMBER: 114:206268
TITLE: Nucleophilic addition of amines to derivatives of unsaturated acids containing 2-alkyl(phenyl)thio groups
AUTHOR(S): Talaikyte, Z.; Vidugiriene, V.; Rasteikiene, L.
CORPORATE SOURCE: Inst. Biokhim., Vilnius, USSR
SOURCE: Chemija (1990), (2), 93-100

CODEN: CHMJES; ISSN: 0235-7216
DOCUMENT TYPE: Journal
LANGUAGE: Russian
GI



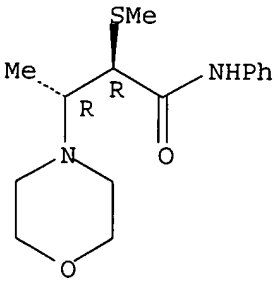
I

AB The title reaction of piperidine or morpholine with RCH:C(SR1)COX (R = Me, Ph; R1 = Me, Ph, CH2CH2Cl; X = NHPh, OMe) is nonstereospecific and gives mixts. of derivs. of erythro- and threo-butanoic acid I (R = Me, R2 = Me, piperidino- or morpholinoethyl; Y = CH2, O) or -phenylpropanoic acid I (R = Ph).

IT **133508-68-6P 133508-69-7P 133508-74-4P**
133508-75-5P 133508-82-4P 133508-83-5P
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of)

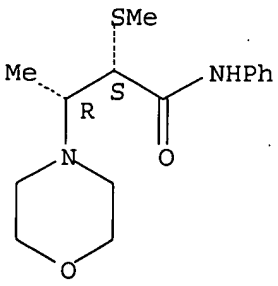
RN 133508-68-6 HCAPLUS
CN 4-Morpholinepropanamide, β-methyl-α-(methylthio)-N-phenyl-, (R*,R*)- (9CI) (CA INDEX NAME)

Relative stereochemistry.



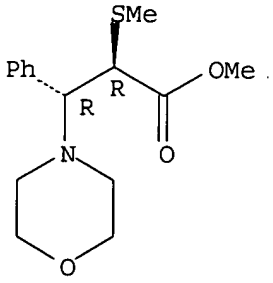
RN 133508-69-7 HCAPLUS
CN 4-Morpholinepropanamide, β-methyl-α-(methylthio)-N-phenyl-, (R*,S*)- (9CI) (CA INDEX NAME)

Relative stereochemistry.



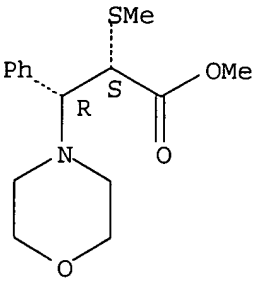
RN 133508-74-4 HCAPLUS
CN 4-Morpholinepropanoic acid, α-(methylthio)-β-phenyl-, methyl ester, (R*,R*)- (9CI) (CA INDEX NAME)

Relative stereochemistry.



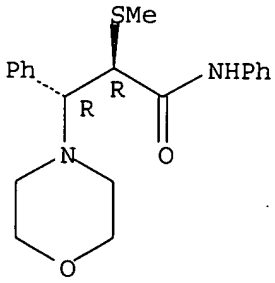
RN 133508-75-5 HCAPLUS
CN 4-Morpholinepropanoic acid, α-(methylthio)-β-phenyl-, methyl ester, (R*,S*)- (9CI) (CA INDEX NAME)

Relative stereochemistry.



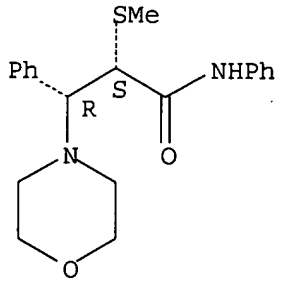
RN 133508-82-4 HCAPLUS
CN 4-Morpholinepropanamide, α-(methylthio)-N,β-diphenyl-, (R*,R*)- (9CI) (CA INDEX NAME)

Relative stereochemistry.



RN 133508-83-5 HCAPLUS
CN 4-Morpholinepropanamide, α-(methylthio)-N,β-diphenyl-, (R*,S*)- (9CI) (CA INDEX NAME)

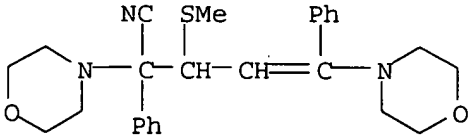
Relative stereochemistry.



L14 ANSWER 5 OF 9 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1990:458617 HCAPLUS
DOCUMENT NUMBER: 113:58617
TITLE: Reactions of organic anions. 168. Reactions of 2-(dialkylamino)arylacetonitriles with acetylenes under basic conditions. A simple synthesis of substituted mono- and diketones
AUTHOR(S): Zdrojewski, T.; Jonczyk, A.
CORPORATE SOURCE: Dep. Chem., Tech. Univ., Warsaw, PL-00-662, Pol.
SOURCE: Synthesis (1990), (3), 224-33
CODEN: SYNTBF; ISSN: 0039-7881
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 113:58617

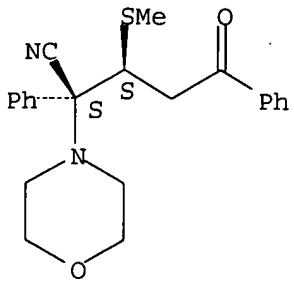
AB The reaction of RCH(CN)NR12 (I; R = Ph, 4-MeC6H4, 4-MeOC6H4; R1 = Me; NR12 = piperidino, morpholino, etc.) with R2C.tplbond.CH (II; R2 = Ph, MeS) gave R12NCR(CN)CH:CHR2 (III) and/or R12NCR(CN)CHR2CH:CRNR12; the product depended on the basicity of the amino group in III. I also added to C-1 of II (R2 = EtO) to give R12NCR(CN)C(OEt):CH2. All these products could be hydrolyzed to give mono- or diketones.

IT **128407-38-5P**
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and hydrolysis of)
RN 128407-38-5 HCAPLUS
CN 4-Morpholineacetonitrile, α-[1-(methylthio)-3-(4-morpholinyl)-3-phenyl-2-propenyl]-α-phenyl- (9CI) (CA INDEX NAME)



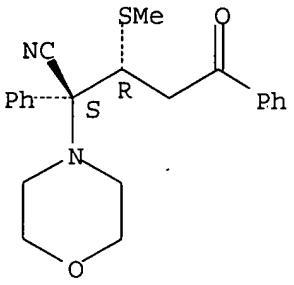
IT **128407-48-7P 128407-49-8P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of)
RN 128407-48-7 HCAPLUS
CN 4-Morpholineacetonitrile, α-[1-(methylthio)-3-oxo-3-phenylpropyl]-α-phenyl-, (R*,R*)- (9CI) (CA INDEX NAME)

Relative stereochemistry.



RN 128407-49-8 HCAPLUS
CN 4-Morpholineacetonitrile, α-[1-(methylthio)-3-oxo-3-phenylpropyl]-α-phenyl-, (R*,S*)- (9CI) (CA INDEX NAME)

Relative stereochemistry.



L14 ANSWER 6 OF 9 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1983:89062 HCAPLUS
DOCUMENT NUMBER: 98:89062
TITLE: Cyclization to form cephem rings and intermediates for this method
INVENTOR(S): Tsuji, Teruji; Hamashima, Yoshio; Yoshioka, Mitsuru; Narisada, Masayuki; Tanida, Hiroshi; Komeno, Taichiro; Nagata, Wataru
PATENT ASSIGNEE(S): Shionogi and Co., Ltd. , Japan
SOURCE: Can., 81 pp. Division of Can. Appl. No. 245,317.
CODEN: CAXXA4
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
CA 1132547	A2	19820928	CA 1979-338132	19791022
JP 51098265	A2	19760830	JP 1975-19612	19750217
JP 51105051	A2	19760917	JP 1975-22229	19750221
JP 51105088	A2	19760917	JP 1975-28452	19750307
JP 60009516	B4	19850311		
JP 51108056	A2	19760925	JP 1975-33808	19750320
JP 58017460	B4	19830407		
CA 1136132	A1	19821123	CA 1976-245317	19760209
ZA 7600809	A	19770126	ZA 1976-809	19760211
AT 353278	B	19791112	AT 1976-1066	19760216

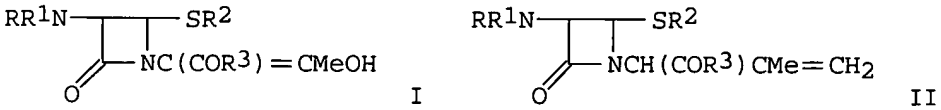
AT 7601066	A	19790415		
IL 56049	A1	19811231	IL 1976-56049	19760216
IL 56050	A1	19811231	IL 1976-56050	19760216
IL 57418	A1	19811231	IL 1976-57418	19760216
IL 57541	A1	19811231	IL 1976-57541	19760216
BE 838656	A1	19760616	BE 1976-164401	19760217
NL 7601613	A	19760819	NL 1976-1613	19760217
NL 190721	B	19940216		
NL 190721	C	19940718		
HU 174070	P	19791028	HU 1976-SI1595	19760217
HU 174387	P	19791228	HU 1976-SI1594	19760217
PL 114457	B1	19810131	PL 1976-212107	19760217
PL 114456	B1	19810131	PL 1976-212109	19760217
PL 114455	B1	19810131	PL 1976-212110	19760217
PL 114624	B1	19810228	PL 1976-212108	19760217
CS 207653	P	19810831	CS 1976-1017	19760217
SU 1187717	A3	19851023	SU 1976-2331355	19760305
FR 2334686	A1	19770708	FR 1977-1587	19770120
FR 2334686	B1	19810123		
FR 2334670	A1	19770708	FR 1977-1588	19770120
FR 2334670	B1	19790824		
FR 2334671	A1	19770708	FR 1977-1589	19770120
FR 2334671	B1	19810123		
FR 2334684	A1	19770708	FR 1977-1590	19770120
FR 2334684	B1	19800328		
SU 791247	D	19801223	SU 1977-2442946	19770126
SU 795463	S	19810107	SU 1977-2446154	19770126
US 4160085	A	19790703	US 1977-856806	19771201
CS 207654	P	19810831	CS 1978-970	19780215
CS 207656	P	19810831	CS 1978-971	19780215
AT 351044	B	19790710	AT 1978-4171	19780608
AT 7804171	A	19781215		
AT 7804170	A	19800715	AT 1978-4170	19780608
AT 361120	B	19810225		
CS 207655	P	19810831	CS 1978-7629	19781122
CA 1077936	A2	19800520	CA 1979-337974	19791019
CA 1095026	A2	19810203	CA 1979-337975	19791019
CA 1144924	A2	19830419	CA 1979-337973	19791019
CH 628030	A	19820215	CH 1980-750	19800130
CH 628031	A	19820215	CH 1980-751	19800130
CH 630074	A	19820528	CH 1980-748	19800130
CH 634579	A	19830215	CH 1980-749	19800130
US 4332722	A	19820601	US 1980-125232	19800227
US 4346218	A	19820824	US 1980-125233	19800227
AT 8002868	A	19810115	AT 1980-2868	19800529
AT 363598	B	19810810		
US 4440683	A	19840403	US 1982-338651	19820111
DK 8200768	A	19820222	DK 1982-768	19820222

PRIORITY APPLN. INFO.:

JP 1975-19612	A	19750217
JP 1975-22229	A	19750221
JP 1975-28452	A	19750307
JP 1975-33808	A	19750320
CA 1976-245317	A3	19760209
DK 1976-619	A	19760216
IL 1976-49048	A3	19760216
IL 1976-56049	A3	19760216
CH 1976-1918	A	19760217
CS 1976-1017		19760217
US 1976-658665	A3	19760217

US 1977-856807	A1	19771201
AT 1976-1066	A	19780608
US 1979-66462	A3	19790813
US 1980-125232	A3	19800227

GI



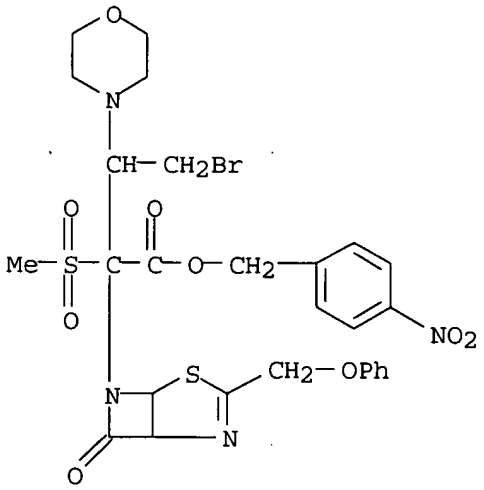
I II

AB Hydroxypropenylazetidinones I [R, R1 = H, acyl; R2 = (un)substituted alkoxycarbonyl, heterocyclylthio, arylthio; RR1R2 = :CR4; R3 = OH, protective group; R4 = aralkyl, aryloxyalkyl] were prepared by ozonolysis of II. The products were converted to 3-hydroxycephems. Thus II [RR1 = C6H4(CO)2-o, R2 = Ac, R3 = OMe] was ozonized and reduced with NaBH4 to give 78% I [RR1 = C6H4(CO)2-o, R2 = Ac, R3 = OMe].

IT **61534-72-3P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of)

RN 61534-72-3 HCAPLUS

CN 4-Thia-2,6-diazabicyclo[3.2.0]hept-2-ene-6-acetic acid, α-[2-bromo-1-(4-morpholinyl)ethyl]-α-(methylsulfonyl)-7-oxo-3-(phenoxymethyl)-, (4-nitrophenyl)methyl ester (9CI) (CA INDEX NAME)



L14 ANSWER 7 OF 9 HCAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 1980:604570 HCAPLUS

DOCUMENT NUMBER: 93:204570

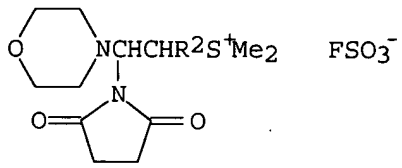
TITLE: Enaminosulfonium salts. 7. A synthesis of α-amino acetals

AUTHOR(S): Vilsmaier, Elmar; Troeger, Wolfgang

CORPORATE SOURCE: Fachber. Chem., Univ. Kaiserslautern, Kaiserslautern, D-6750, Fed. Rep. Ger.

SOURCE: Synthesis (1980), (6), 466-9
CODEN: SYNTBF; ISSN: 0039-7881

DOCUMENT TYPE: Journal
LANGUAGE: German
OTHER SOURCE(S): CASREACT 93:204570
GI



I

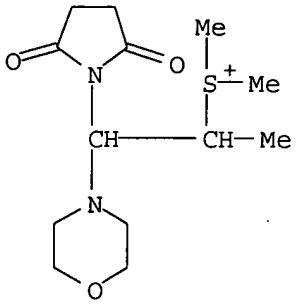
AB Reaction of the enamines RR1NCH:CHR2 (NRR1 = morpholino, R2 = Me, Et, Ph) with dimethylsuccinimidosulfonium fluorosulfate gave 42-94% RR1NCH:CR2S+Me2 FSO3- and 5-28% I (R = Me, Et). Alcoholysis of I gave the salts (R3O)2CHCHR2N+HRR1 FSO3- (R3 = Me, Et) which were deprotonated to (R3O)2CHCHR2NRR1.

IT **75199-59-6P 75199-61-0P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of)

RN 75199-59-6 HCAPLUS
CN Sulfonium, [2-(2,5-dioxo-1-pyrrolidinyl)-1-methyl-2-(4-morpholinyl)ethyl]dimethyl-, (E)-, fluorosulfate (9CI) (CA INDEX NAME)

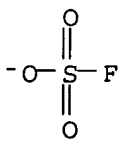
CM 1

CRN 75199-58-5
CMF C13 H23 N2 O3 S



CM 2

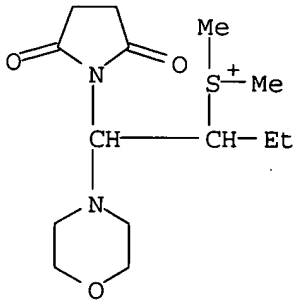
CRN 15181-47-2
CMF F O3 S



RN 75199-61-0 HCAPLUS
CN Sulfonium, [1-[(2,5-dioxo-1-pyrrolidinyl)(4-morpholinyl)methyl]propyl]dimethyl-, fluorosulfate (9CI) (CA INDEX NAME)

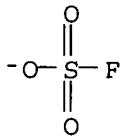
CM 1

CRN 75199-60-9
CMF C14 H25 N2 O3 S

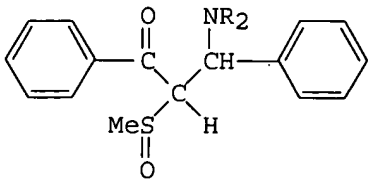


CM 2

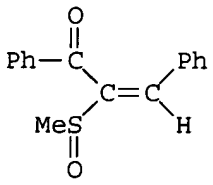
CRN 15181-47-2
CMF F O3 S



L14 ANSWER 8 OF 9 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1979:574952 HCAPLUS
DOCUMENT NUMBER: 91:174952
TITLE: Thermolysis of Mannich bases from β-oxo sulfoxides, benzaldehyde and secondary amines
AUTHOR(S): Boehme, Horst; Clement, Bernd
CORPORATE SOURCE: Pharm.-Chem. Inst., Philipps-Univ., Marburg, 355, Fed. Rep. Ger.
SOURCE: Archiv der Pharmazie (Weinheim, Germany) (1979), 312(6), 531-4
CODEN: ARPMAS; ISSN: 0365-6233
DOCUMENT TYPE: Journal
LANGUAGE: German
GI



I



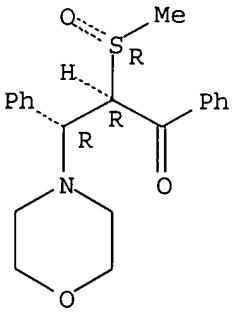
II

AB Stable Mannich bases I [R = Me, R2 = (CH2)4, CH2CH2OCH2CH2] were obtained as mixts. of 4 diastereoisomeric forms, stipulated by the 3 chiral centers, by condensation of PhCOCH2S(O)Me with PhCHO and HNR2. Amine elimination occurred on heating I (R = Me) >180° to give a single (E) diastereomer of the propenone II.

IT **71679-38-4P 71698-82-3P 71698-83-4P 71698-85-6P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of)

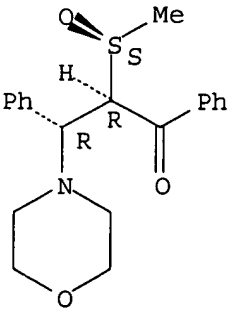
RN 71679-38-4 HCAPLUS
CN 1-Propanone, 2-(methylsulfinyl)-3-(4-morpholinyl)-1,3-diphenyl-, [2R*(R*),3R*]- (9CI) (CA INDEX NAME)

Relative stereochemistry.



RN 71698-82-3 HCAPLUS
CN 1-Propanone, 2-(methylsulfinyl)-3-(4-morpholinyl)-1,3-diphenyl-, [2R*(S*),3R*]- (9CI) (CA INDEX NAME)

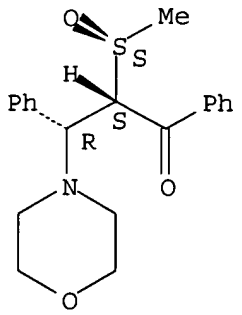
Relative stereochemistry.



RN 71698-83-4 HCAPLUS
CN 1-Propanone, 2-(methylsulfinyl)-3-(4-morpholinyl)-1,3-diphenyl-,

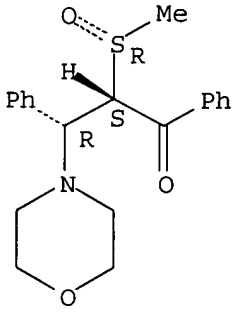
[2R*(R*),3S*]- (9CI) (CA INDEX NAME)

Relative stereochemistry.



RN 71698-85-6 HCAPLUS
CN 1-Propanone, 2-(methylsulfinyl)-3-(4-morpholinyl)-1,3-diphenyl-, [2R*(S*),3S*]- (9CI) (CA INDEX NAME)

Relative stereochemistry.



L14 ANSWER 9 OF 9 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1977:55466 HCAPLUS
DOCUMENT NUMBER: 86:55466
TITLE: Azetidine derivatives
INVENTOR(S): Tsuji, Teruji; Hamashima, Yoshio; Yoshioka, Mitsuru; Narisada, Masayuki; Tanida, Hiroshi; Komeno, Taichiro; Nagata, Wataru
PATENT ASSIGNEE(S): Shionogi and Co., Ltd., Japan
SOURCE: Ger. Offen., 126 pp.
CODEN: GWXXBX
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 2606278	A1	19760826	DE 1976-2606278	19760217
DE 2606278	C2	19890503		
JP 51098265	A2	19760830	JP 1975-19612	19750217
JP 51105051	A2	19760917	JP 1975-22229	19750221
JP 51105088	A2	19760917	JP 1975-28452	19750307

JP 60009516	B4	19850311		
JP 51108056	A2	19760925	JP 1975-33808	19750320
JP 58017460	B4	19830407		
ZA 7600809	A	19770126	ZA 1976-809	19760211
DK 7600619	A	19760818	DK 1976-619	19760216
DK 156575	B	19890911		
DK 156575	C	19900205		
SE 7601715	A	19760818	SE 1976-1715	19760216
SE 421691	B	19820125		
SE 421691	C	19820506		
AT 353278	B	19791112	AT 1976-1066	19760216
AT 7601066	A	19790415		
IL 49048	A1	19811231	IL 1976-49048	19760216
IL 56049	A1	19811231	IL 1976-56049	19760216
IL 56050	A1	19811231	IL 1976-56050	19760216
IL 57418	A1	19811231	IL 1976-57418	19760216
IL 57541	A1	19811231	IL 1976-57541	19760216
BE 838656	A1	19760616	BE 1976-164401	19760217
NL 7601613	A	19760819	NL 1976-1613	19760217
NL 190721	B	19940216		
NL 190721	C	19940718		
DD 124986	C	19770323	DD 1976-191283	19760217
ES 445250	A1	19770616	ES 1976-445250	19760217
FR 2334669	A1	19770708	FR 1976-4318	19760217
FR 2334669	B1	19811231		
AU 7611181	A1	19770825	AU 1976-11181	19760217
AU 508160	B2	19800313		
DD 127899	C	19771019	DD 1976-195993	19760217
DD 127900	C	19771019	DD 1976-195995	19760217
DD 127901	C	19771019	DD 1976-195997	19760217
DD 127902	C	19771019	DD 1976-195998	19760217
US 4079181	A	19780314	US 1976-658665	19760217
GB 1548641	A	19790718	GB 1976-6187	19760217
HU 174070	P	19791028	HU 1976-SI1595	19760217
HU 174387	P	19791228	HU 1976-SI1594	19760217
RO 75006	P	19801030	RO 1976-94586	19760217
RO 74958	P	19801030	RO 1976-94587	19760217
PL 114457	B1	19810131	PL 1976-212107	19760217
PL 114456	B1	19810131	PL 1976-212109	19760217
PL 114455	B1	19810131	PL 1976-212110	19760217
PL 114624	B1	19810228	PL 1976-212108	19760217
RO 68460	P	19810817	RO 1976-84836	19760217
CS 207653	P	19810831	CS 1976-1017	19760217
CH 627160	A	19811231	CH 1976-1918	19760217
SU 1187717	A3	19851023	SU 1976-2331355	19760305
RO 74936	P	19801030	RO 1976-94585	19760717
FR 2334686	A1	19770708	FR 1977-1587	19770120
FR 2334686	B1	19810123		
FR 2334670	A1	19770708	FR 1977-1588	19770120
FR 2334670	B1	19790824		
FR 2334671	A1	19770708	FR 1977-1589	19770120
FR 2334671	B1	19810123		
FR 2334684	A1	19770708	FR 1977-1590	19770120
FR 2334684	B1	19800328		
SU 791247	D	19801223	SU 1977-2442946	19770126
SU 795463	S	19810107	SU 1977-2446154	19770126
US 4160085	A	19790703	US 1977-856806	19771201
CS 207654	P	19810831	CS 1978-970	19780215
CS 207656	P	19810831	CS 1978-971	19780215

AT 351044	B	19790710	AT 1978-4171	19780608
AT 7804171	A	19781215		
AT 7804170	A	19800715	AT 1978-4170	19780608
AT 361120	B	19810225		
CS 207655	P	19810831	CS 1978-7629	19781122
SE 7907811	A	19790920	SE 1979-7811	19790920
SE 444811	B	19860512		
SE 444811	C	19860821		
SE 7907812	A	19790920	SE 1979-7812	19790920
SE 434950	B	19840827		
SE 434950	C	19841206		
SE 7907813	A	19790920	SE 1979-7813	19790920
SE 434637	B	19840806		
SE 434637	C	19841115		
CH 628030	A	19820215	CH 1980-750	19800130
CH 628031	A	19820215	CH 1980-751	19800130
CH 630074	A	19820528	CH 1980-748	19800130
CH 634579	A	19830215	CH 1980-749	19800130
US 4332722	A	19820601	US 1980-125232	19800227
US 4346218	A	19820824	US 1980-125233	19800227
AT 8002868	A	19810115	AT 1980-2868	19800529
AT 363598	B	19810810		
US 4440683	A	19840403	US 1982-338651	19820111
DK 8200768	A	19820222	DK 1982-768	19820222

PRIORITY APPLN. INFO.:

JP 1975-19612	A	19750217
JP 1975-22229	A	19750221
JP 1975-28452	A	19750307
JP 1975-33808	A	19750320
DK 1976-619	A	19760216
IL 1976-49048	A3	19760216
IL 1976-56049	A3	19760216
CH 1976-1918	A	19760217
CS 1976-1017		19760217
US 1976-658665	A3	19760217
US 1977-856807	A1	19771201
AT 1976-1066	A	19780608
US 1979-66462	A3	19790813
US 1980-125232	A3	19800227

OTHER SOURCE(S): CASREACT 86:55466

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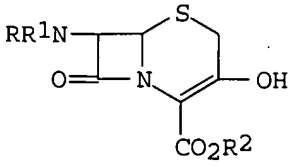

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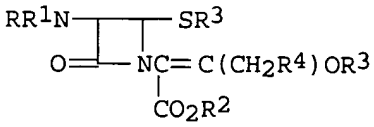
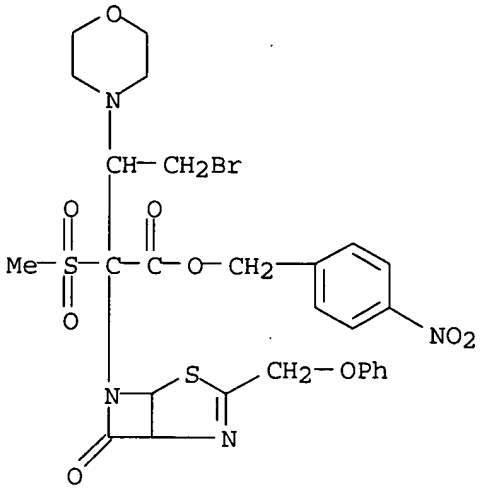


II

AB Hydroxycephems I (NRR1 = phthalimido, NHCOCH2OPh, NHCOCH2Ph; R2 = Me, CH2CCl3, CH2C6H4NO2-4, CHPh2, CH2CCl3, CH2Ph) were prepared by protecting the azetidinones II (R3 = R4 = H) with ClCO2CH2Ph or cyclopropylmethyl chloroformate, for example, treating II (R3 = e.g., cyclopropylmethoxycarbonyl, R4 = H) with Br, cleaving the protective groups from II (R3 = e.g., cyclopropylmethoxycarbonyl, R4 = Br), and cyclizing II (R3 = H, R4 = Br) with acid.

IT **61534-72-3P**

RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of)
RN 61534-72-3 HCAPLUS
CN 4-Thia-2,6-diazabicyclo[3.2.0]hept-2-ene-6-acetic acid, α-[2-bromo-1-(4-morpholinyl)ethyl]-α-(methylsulfonyl)-7-oxo-3-(phenoxymethyl)-, (4-nitrophenyl)methyl ester (9CI) (CA INDEX NAME)

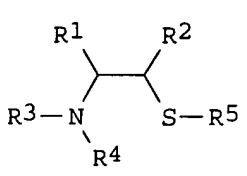


=> d l15 ibib abs hitstr tot

L15 ANSWER 1 OF 12 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 2005:354977 HCAPLUS
DOCUMENT NUMBER: 142:463603
TITLE: Aminoethanethiol derivatives as highly efficient chiral ligands in asymmetric reactions, especially in enantioselective nucleophilic addition of carbonyls with alkylmetals
INVENTOR(S): Yang, Denggui; Liu, Ta; Chen, Nanguang
PATENT ASSIGNEE(S): Haimen Hurju Pharmaceutical Co., Ltd., Peop. Rep. China
SOURCE: Faming Zhuanli Shenqing Gongkai Shuomingshu, 9 pp.
CODEN: CNXXEV
DOCUMENT TYPE: Patent
LANGUAGE: Chinese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
CN 1434034	A	20030806	CN 2001-143059	20011207

PRIORITY APPLN. INFO.: CN 2001-143059 20011207
OTHER SOURCE(S): CASREACT 142:463603
GI



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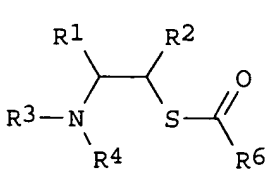
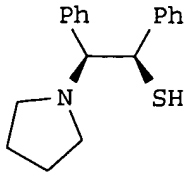


II



III

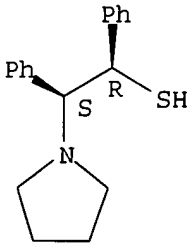
AB The invention relates to aminoethanethiol derivs. I and II [wherein R1, R2 = alkyl or aryl; R3, R4 = alkyl; R5, R6 = H or alkyl; etc.] and their applications as chiral ligands in asym. reactions, especially in asym. reduction of aldehydes through their organometallic (Zn, Cu and Ti) complexes and in enantioselective nucleophilic addition of carbonyl compds. with alkylmetals. The remarkably high asym.-induction efficiency of the invented compds. were demonstrated by three examples such as III using addition reaction of benzaldehyde with diethylzinc as probe. As little as 0.02% (molar ratio of ligand to substrate) of the ligands were enough to achieve >99% ee.

IT **571148-35-1**
RL: CAT (Catalyst use); USES (Uses)
(aminoethanethiol derivs. as highly efficient chiral ligands in asym. reactions)

RN 571148-35-1 HCAPLUS

CN 1-Pyrrolidineethanethiol, α,β-diphenyl-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



L15 ANSWER 2 OF 12 HCAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 2005:130245 HCAPLUS

DOCUMENT NUMBER: 142:373291

TITLE: New β-amino thiols as efficient catalysts for highly enantioselective alkenylzinc addition to aldehydes

AUTHOR(S): Tseng, Shi-Liang; Yang, Teng-Kuei

CORPORATE SOURCE: Department of Chemistry, National Chung-Hsing University, Taichung, 40227, Peop. Rep. China

SOURCE: Tetrahedron: Asymmetry (2005), 16(4), 773-782
CODEN: TASYE3; ISSN: 0957-4166

PUBLISHER: Elsevier B.V.

DOCUMENT TYPE: Journal

LANGUAGE: English

OTHER SOURCE(S): CASREACT 142:373291

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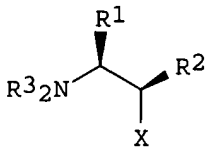

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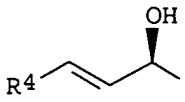


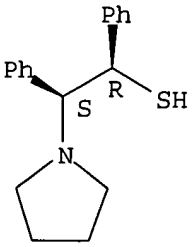
II

AB A series of new optically active β-amino thiols and thiol acetates I [X = HS, MeCOS; R1, R2 = Me2CH, Ph; R32 = (CH2)4, (CH2)5], prepared from the simple natural amino acid (S)-(-)-valine, were found to be effective catalysts for the enantioselective addition of alkenylzinc reagents R4CH:CHZnEt (R4 = n-Bu, Me3C, n-hexyl, Ph) to aldehydes R5CHO (R5 = cyclohexyl, Ph, 2-ClC6H4, 4-MeOC6H4, PhCH:CH) and thereby providing an efficient route to chiral (E)-allylic alcs. II with ees of up to >99%.

IT **571148-35-1P 757243-33-7P 757243-42-8P**
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)
(preparation of β-amino-substituted alcs., thiols and thiol acetates as chiral catalysts for enantioselective alkenylzinc addition to aldehydes)

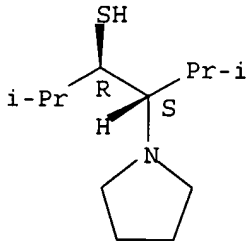
RN 571148-35-1 HCAPLUS
CN 1-Pyrrolidineethanethiol, α,β-diphenyl-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



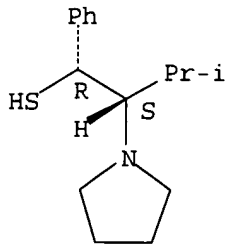
RN 757243-33-7 HCAPLUS
CN 1-Pyrrolidineethanethiol, α,β-bis(1-methylethyl)-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (+).



RN 757243-42-8 HCAPLUS
CN 1-Pyrrolidineethanethiol, β-(1-methylethyl)-α-phenyl-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



REFERENCE COUNT: 28 THERE ARE 28 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L15 ANSWER 3 OF 12 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 2004:920913 HCAPLUS
DOCUMENT NUMBER: 142:74307
TITLE: The application of chiral amino thiols as catalysts in the enantioselective addition of diethylzinc to aldehydes
AUTHOR(S): Tseng, Shi-Liang; Yang, Teng-Kuei
CORPORATE SOURCE: Department of Chemistry, National Chung-Hsing University, Taichung, 40227, Taiwan
SOURCE: Tetrahedron: Asymmetry (2004), 15(22), 3375-3380
CODEN: TASYE3; ISSN: 0957-4166
PUBLISHER: Elsevier B.V.
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 142:74307
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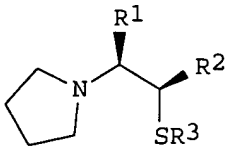


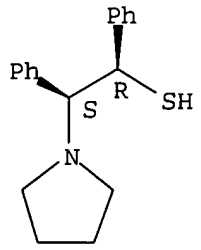
I

AB Starting from (S)-(-)-valine, a series of new chiral amino thiol and corresponding thioacetate ligands I (R1, R2 = Me2CH, Ph; R3 = H, MeCO) was prepared in an efficient manner and applied in the asym. diethylzinc addition to aldehydes R4CHO (R4 = Ph, 2-MeOC6H4, 2-naphthyl, n-octyl, etc.) to afford alcs. (R)-R4CH(OH)Et with excellent enantioselectivity (up to 99% ee) and with a catalytic loading as little as 0.02 mol % [for the amino thiol I (R1 = R2 = Ph; R3 = H)].

IT **571148-35-1P 757243-33-7P 757243-42-8P**
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)
(preparation of chiral amino thiols and their use as catalysts in enantioselective addition of diethylzinc to aldehydes)

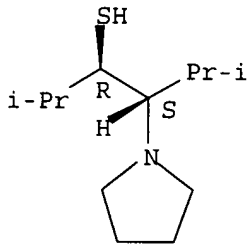
RN 571148-35-1 HCAPLUS
CN 1-Pyrrolidineethanethiol, α,β-diphenyl-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



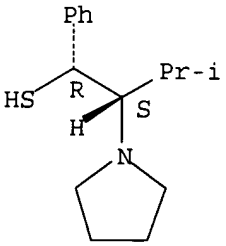
RN 757243-33-7 HCAPLUS
CN 1-Pyrrolidineethanethiol, α,β-bis(1-methylethyl)-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (+).



RN 757243-42-8 HCAPLUS
CN 1-Pyrrolidineethanethiol, β-(1-methylethyl)-α-phenyl-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



REFERENCE COUNT: 28 THERE ARE 28 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L15 ANSWER 4 OF 12 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 2004:759870 HCAPLUS
DOCUMENT NUMBER: 141:277501
TITLE: Preparation of 2-aminoethanethiol compounds as efficient catalysts for asymmetric addition reaction
INVENTOR(S): Yang, Teng-Kuei; Tseng, Shi-Liang; Liu, To; Chen, Nan-Kuang
PATENT ASSIGNEE(S): Taiwan
SOURCE: U.S. Pat. Appl. Publ., 15 pp., Cont.-in-part of U.S. Pat. Appl. 2003 153,781.

CODEN: USXXCO
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 2004181057	A1	20040916	US 2004-807710	20040323
US 2003153781	A1	20030814	US 2002-39557	20020108
US 6861536	B2	20050301		

PRIORITY APPLN. INFO.: US 2002-39557 A2 20020108
OTHER SOURCE(S): MARPAT 141:277501

AB The present invention discloses aminothiol compds. having a general formula R3R4NCH(R1)CH(R2)SR5 (wherein R1-R4 = aryl, C1-9 alkyl; or R3, R4 and N form a three- to eight-membered heterocycle; R5 = H, C1-6 alkyl). Such compds. can perform as superior catalysts for the synthesis of chiral secondary alcs. by asym. addition reaction of organic metal compds. such organozinc compound and aldehyde. According to the present invention, the aminothiol compds. are needed only less than 0.02% based on main reactants to obtain enantioselectivity higher than 98% enantiomeric excess, whereby the asym. reactions can become very economic. Thus, cycloalkylation of (2R,3S)-3-amino-4-methylpentan-2-ol by 1,4-dibromobutane in the presence of Na2CO3 in MeCN under refluxing for 12 h gave (2R,3S)-4-methyl-3-(1-pyrrolidinyl)pentan-2-ol which was treated with MeSO2Cl and Et3N in CH2Cl2 for 2 h at 0° for 2 h, concentrated, and reacted with thioacetic acid in benzene at room temperature for 12 h to give 20% (2R,3S)-4-methyl-3-(1-pyrrolidinyl)-2-thioacetylpentane (I) and 40% (3R,4S)-2-methyl-4-(1-pyrrolidinyl)-3-thioacetylpentane (II). I or II was reduced by LiAlH4 in Et2O at 0° for 1 h to give (2R,3S)-4-methyl-3-(1-pyrrolidinyl)pentane-2-thiol or (3R,4S)-2-methyl-4-(1-pyrrolidinyl)pentane-3-thiol (III) in 80% yield. Asym. addition reaction of benzaldehyde with Et2Zn in toluene in the presence of 0.05 mequiv. (equivalence concentration)

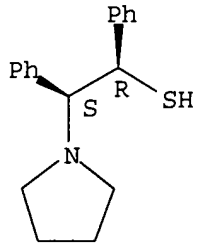
III

at -20° for 12 h gave (R)-2-phenylpropanol (99.6% ee). Chiral (R)-1-phenyl-2-alken-1-ols were also prepared from butylacetylene and hexylacetylene by monohydroboration of alkynes with BH3.SMe2 and transmetalation of boron to zinc with diethylzinc and asym. addition reaction with benzaldehyde or derivs. using the aminothiol catalysts.

IT **571148-35-1P**, (1R,2S)-1,2-Diphenyl-2-pyrrolidin-1-ylethane-1-thiol
757242-87-8P, (2R,3S)-4-Methyl-3-(1-pyrrolidinyl)pentane-2-thiol
757242-90-3P, (3R,4S)-2-Methyl-4-(1-pyrrolidinyl)pentane-3-thiol
757243-14-4P, (3S,4R)-2-Methyl-3-(1-pyrrolidinyl)octane-4-thiol
757243-19-9P, (3R,4S)-2-Methyl-4-(1-pyrrolidinyl) octane-3-thiol
757243-33-7P, (3R,4S)-2,5-Dimethyl-4-(1-pyrrolidinyl)hexane-3-thiol **757243-42-8P**, (1R,2S)-3-Methyl-1-phenyl-2-(1-pyrrolidinyl)butane-1-thiol
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)
(catalyst; preparation of 2-aminoethanethiol compds. as catalysts for asym. addition reaction of organic metal compound with aldehydes)

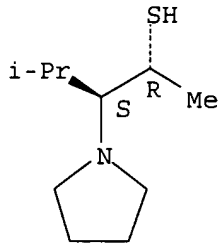
RN 571148-35-1 HCAPLUS
CN 1-Pyrrolidineethanethiol, α,β-diphenyl-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



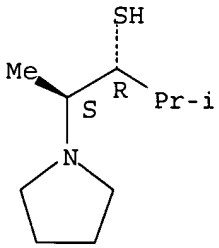
RN 757242-87-8 HCAPLUS
CN 1-Pyrrolidineethanethiol, α-methyl-β-(1-methylethyl)-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (+).



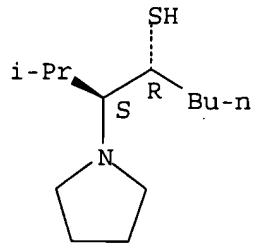
RN 757242-90-3 HCAPLUS
CN 1-Pyrrolidineethanethiol, β-methyl-α-(1-methylethyl)-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



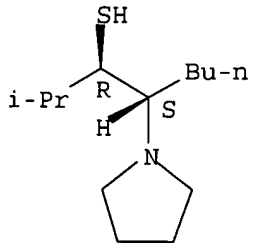
RN 757243-14-4 HCAPLUS
CN 1-Pyrrolidineethanethiol, α-butyl-β-(1-methylethyl)-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (+).



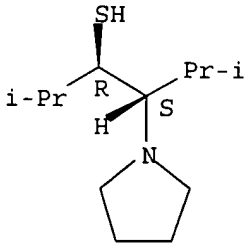
RN 757243-19-9 HCAPLUS
CN 1-Pyrrolidineethanethiol, β-butyl-α-(1-methylethyl)-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (+).



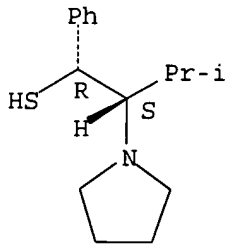
RN 757243-33-7 HCAPLUS
CN 1-Pyrrolidineethanethiol, α,β-bis(1-methylethyl)-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (+).



RN 757243-42-8 HCAPLUS
CN 1-Pyrrolidineethanethiol, β-(1-methylethyl)-α-phenyl-, (αR,βS)- (9CI) (CA INDEX NAME)

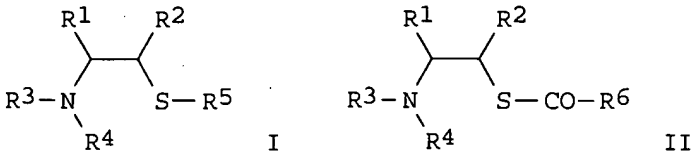
Absolute stereochemistry. Rotation (-).



L15 ANSWER 5 OF 12 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 2003:633325 HCAPLUS
DOCUMENT NUMBER: 139:149522
TITLE: Aminothiol compounds and acylated derivatives thereof
INVENTOR(S): Yang, Teng-Kuei; Chen, Nan-Kuang; Liu, To
PATENT ASSIGNEE(S): National Chung-Hsing University, Taiwan
SOURCE: U.S. Pat. Appl. Publ., 5 pp.
CODEN: USXXCO
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 2003153781	A1	20030814	US 2002-39557	20020108
US 6861536	B2	20050301		
US 2004049033	A1	20040311	US 2003-650020	20030826
US 6965038	B2	20051115		
US 2004181057	A1	20040916	US 2004-807710	20040323
PRIORITY APPLN. INFO.:			US 2002-39557	A3 20020108
OTHER SOURCE(S):	MARPAT 139:149522			

GI

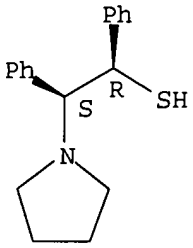


AB The present invention discloses aminothiol compds. and acylated derivs. I and II (R1, R2, R3, R4 = C1-9-alkyl or NR3R4 = 3-8-membered heterocycle, R5 and R6 = H, C1-6-alkyl) are substitutable ligands. For example, 1,2-diphenyl-2-pyrrolidinylethanethiol was prepared by the reaction of (1R,2S)-1,2-diphenyl-2-aminoethanol with 1,4-dibromobutane, followed by reaction of MeSO3Cl and reduction by LiAlH4. Such compds. can perform as superior catalysts in asym. addition reactions of organic Zn and aldehyde. According to the present invention, the compds. needed only <0.02% of main reactants to obtain enantioselectivity >99% enantiomeric excess, whereby the asym. reactions can become very economic.

IT **571148-35-1P**
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation);

USES (Uses)
(preparation as asym. addition catalyst with organozinc complexes with aldehydes)
RN 571148-35-1 HCAPLUS
CN 1-Pyrrolidineethanethiol, α,β-diphenyl-, (αR,βS)-
(9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



REFERENCE COUNT: 5 THERE ARE 5 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L15 ANSWER 6 OF 12 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 2001:636044 HCAPLUS
DOCUMENT NUMBER: 135:195495
TITLE: Preparation of 2-oxo-1-pyrrolidine derivatives and their anticonvulsant activity
INVENTOR(S): Differding, Edmond; Kenda, Benoit; Lallemand, Benedicte; Matagne, Alain; Michel, Philippe; Pasau, Patrick; Talaga, Patrice
PATENT ASSIGNEE(S): UCB, S.A., Belg.
SOURCE: PCT Int. Appl., 100 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 3
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2001062726	A2	20010830	WO 2001-EP1992	20010221
WO 2001062726	A3	20020117		
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW				
RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG				
CA 2401033	AA	20010830	CA 2001-2401033	20010221
AU 2001052144	A5	20010903	AU 2001-52144	20010221
EP 1265862	A2	20021218	EP 2001-925354	20010221
EP 1265862	B1	20050921		
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR				
BR 2001008664	A	20030429	BR 2001-8664	20010221

JP 2003523996	T2	20030812	JP 2001-561734		20010221
NZ 520448	A	20040326	NZ 2001-520448		20010221
EP 1447399	A1	20040818	EP 2004-7733		20010221
EP 1447399	B1	20060503			
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR					
EP 1452524	A1	20040901	EP 2004-7878		20010221
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ES 2231501	T3	20050516	ES 2001-1940256		20010221
EP 1577295	A1	20050921	EP 2004-30940		20010221
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EP 1577296	A1	20050921	EP 2005-12174		20010221
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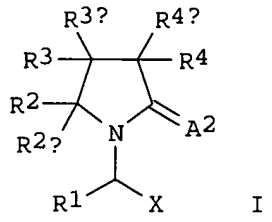
CN 1680314	A	20051012	CN 2005-10071308		20010221
AT 304999	E	20051015	AT 2001-925354		20010221
EP 1604979	A1	20051214	EP 2005-13657		20010221
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, LV, FI, MK, CY, AL, TR					
CN 1740151	A	20060301	CN 2005-10099952		20010221
CN 1740150	A	20060301	CN 2005-10099953		20010221
ES 2248307	T3	20060316	ES 2001-1925354		20010221
ZA 2002005671	A	20031110	ZA 2002-5671		20020716
ZA 2002005837	A	20031104	ZA 2002-5837		20020722
BG 107004	A	20030430	BG 2002-107004		20020814
US 2003120080	A1	20030626	US 2002-204266		20020820
US 6784197	B2	20040831			
NO 2002003997	A	20021022	NO 2002-3997		20020822
HK 1052516	A1	20060210	HK 2003-104916		20030709
US 2004087646	A1	20040506	US 2003-694090		20031028
US 6806287	B2	20041019			
US 2004116507	A1	20040617	US 2003-693917		20031028
US 6911461	B2	20050628			
EP 1477478	A2	20041117	EP 2004-8270		20040406
EP 1477478	A3	20041124			
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR					
US 2005171187	A1	20050804	US 2005-43145		20050127
US 2005171188	A1	20050804	US 2005-43176		20050127
AU 2005203271	A1	20050818	AU 2005-203271		20050726
AU 2005203275	A1	20050818	AU 2005-203275		20050726
AU 2005203276	A1	20050818	AU 2005-203276		20050726
NO 2005003644	A	20021022	NO 2005-3644		20050727
NO 2005003645	A	20021022	NO 2005-3645		20050727
JP 2006022107	A2	20060126	JP 2005-217433		20050727
JP 2006022108	A2	20060126	JP 2005-217442		20050727
PRIORITY APPLN. INFO.:			GB 2000-4297	A	20000223
			AU 2001-52144	A3	20010221
			CN 2001-805445	A3	20010221
			CN 2005-10071308	A3	20010221
			EP 2001-925354	A3	20010221
			EP 2001-940256	A3	20010221
			JP 2001-561734	A3	20010221
			WO 2001-EP1992	W	20010221
			US 2002-204266	A3	20020820
			US 2003-693917	A3	20031028
			EP 2004-8270	A3	20040406

OTHER SOURCE(S): MARPAT 135:195495
GI



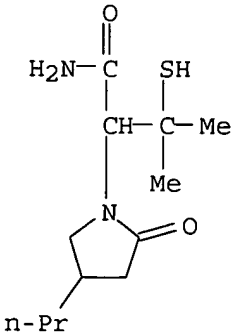
I

AB The title 2-oxo-1-pyrrolidine derivs. I [X = CA1NR5R6, CA1OR7, CA1R8, cyano; A1, A2 = O, S, NR9; R1 = H, alkyl, aryl, CH2R1; R2-R4 = H, halo, OH, SH, etc.; R2a, R3a, R4a = H, halo, alkyl, alkenyl, alkynyl, aryl; R5-R7, R9 = H, OH, alkyl, aryl, heterocyclyl; R8 = H, OH, SH, etc.] were prepared E.g., (2S)-2-[2-oxo-4-(phenoxymethyl)-1-pyrrolidinyl]butanamide was prepared I are particularly suited for treating neurol. disorders such as epilepsy.

IT **357337-34-9P**
RL: BAC (Biological activity or effector, except adverse); BSU (Biological study, unclassified); SPN (Synthetic preparation); THU (Therapeutic use); BIOL (Biological study); PREP (Preparation); USES (Uses)
(preparation of 2-oxo-1-pyrrolidine derivs. and their anticonvulsant activity)

RN 357337-34-9 HCAPLUS

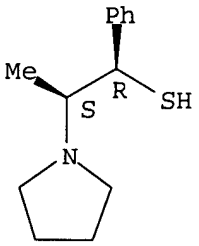
CN 1-Pyrrolidineacetamide, α-(1-mercapto-1-methylethyl)-2-oxo-4-propyl- (9CI) (CA INDEX NAME)



L15 ANSWER 7 OF 12 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1997:39785 HCAPLUS
DOCUMENT NUMBER: 126:131036
TITLE: Chiral β-amino thiol catalysts for the enantioselective addition of diethylzinc to aldehydes
AUTHOR(S): Kang, Jahyo; Kim, Jeong Whan; Lee, Jun Won; Kim, Dong Soo; Kim, Joo In
CORPORATE SOURCE: Dep. Chem., Sogang Univ., Seoul, 121-742, S. Korea
SOURCE: Bulletin of the Korean Chemical Society (1996),

17(12), 1135-1142
CODEN: BKCSDE; ISSN: 0253-2964
PUBLISHER: Korean Chemical Society
DOCUMENT TYPE: Journal
LANGUAGE: English
AB Reaction of diethylzinc with α-branched aldehydes in the presence of a catalytic amount (5 mol %) of various β-amino thiols in toluene or ether provided the corresponding secondary alcs. in outstanding ee. Detailed preparative procedure for the β-amino thiols are presented.
IT **166031-50-1P**
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)
(enantioselective addition of diethylzinc to aldehydes using chiral β-amino thiol catalysts)
RN 166031-50-1 HCAPLUS
CN 1-Pyrrolidineethanethiol, β-methyl-α-phenyl-, [R-(R*,S*)]- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



REFERENCE COUNT: 29 THERE ARE 29 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L15 ANSWER 8 OF 12 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1995:86424 HCAPLUS
DOCUMENT NUMBER: 123:142957
TITLE: Enantioselective addition of diethylzinc to α-branched aldehydes
AUTHOR(S): Kang, Jahyo; Lee, Jun Won; Kim, Joo In
CORPORATE SOURCE: Department of Chemistry, Sogang University, Seoul, 121-742, S. Korea
SOURCE: Journal of the Chemical Society, Chemical Communications (1994), (17), 2009-10
CODEN: JCCCAT; ISSN: 0022-4936
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 123:142957
AB Reaction of diethylzinc with α-branched aldehydes in the presence of a catalytic amount of (1R,2S)-(-)-1-phenyl-2-piperidinopropane-1-thiol provided the corresponding secondary alcs. in almost 100% enantiomeric excess.
IT **166031-50-1P**
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)
(as ligand catalyst for enantioselective addition of diethylzinc to α-branched aldehydes)
RN 166031-50-1 HCAPLUS
CN 1-Pyrrolidineethanethiol, β-methyl-α-phenyl-, [R-(R*,S*)]-

AUTHOR(S): Trost, Barry M.; Shibata, Tohru
CORPORATE SOURCE: Dep. Chem., Univ. Wisconsin, Madison, WI, 53706, USA
SOURCE: Journal of the American Chemical Society (1982), 104(11), 3225-8
CODEN: JACSAT; ISSN: 0002-7863
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 96:217316

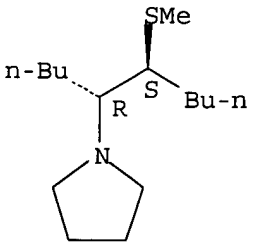
AB The selectivity of Me2(MeS)S+.BF4- (DMTSF) permits simultaneous addition of a nitrogen nucleophile and sulfur electrophile across a double bond in a stereospecifically trans fashion. Amines, azide and nitrite serve as nitrogen nucleophiles. By appropriate choice of the nitrogen nucleophiles, either Markovnikov or anti-Markovnikov addition is possible. The method serves as an equivalent of nucleophilic addition to or substitution of an olefin. The adducts were converted to oxazolines which serve as the equivalent of a cis hydroxyamination or to aziridines.

IT **81230-62-8P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of)

RN 81230-62-8 HCAPLUS

CN Pyrrolidine, 1-[1-butyl-2-(methylthio)hexyl]-, (R*,S*)- (9CI) (CA INDEX NAME)

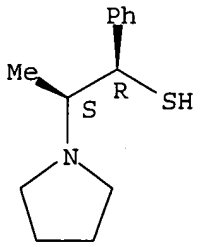
Relative stereochemistry.



L15 ANSWER 11 OF 12 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1980:604570 HCAPLUS
DOCUMENT NUMBER: 93:204570
TITLE: Enaminosulfonium salts. 7. A synthesis of α-amino acetals
AUTHOR(S): Vilsmaier, Elmar; Troeger, Wolfgang
CORPORATE SOURCE: Fachber. Chem., Univ. Kaiserslautern, Kaiserslautern, D-6750, Fed. Rep. Ger.
SOURCE: Synthesis (1980), (6), 466-9
CODEN: SYNTBF; ISSN: 0039-7881
DOCUMENT TYPE: Journal
LANGUAGE: German
OTHER SOURCE(S): CASREACT 93:204570
GI

(9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).

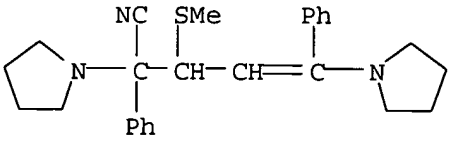


L15 ANSWER 9 OF 12 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1990:458617 HCAPLUS
DOCUMENT NUMBER: 113:58617
TITLE: Reactions of organic anions. 168. Reactions of 2-(dialkylamino)arylacetonitriles with acetylenes under basic conditions. A simple synthesis of substituted mono- and diketones
AUTHOR(S): Zdrojewski, T.; Jonczyk, A.
CORPORATE SOURCE: Dep. Chem., Tech. Univ., Warsaw, PL-00-662, Pol.
SOURCE: Synthesis (1990), (3), 224-33
CODEN: SYNTBF; ISSN: 0039-7881
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 113:58617

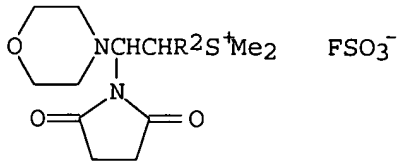
AB The reaction of RCH(CN)NR12 (I; R = Ph, 4-MeC6H4, 4-MeOC6H4; R1 = Me; NR12 = piperidino, morpholino, etc.) with R2C.tplbond.CH (II; R2 = Ph, MeS) gave R12NCR(CN)CH:CHR2 (III) and/or R12NCR(CN)CHR2CH:CRNR12; the product depended on the basicity of the amino group in III. I also added to C-1 of II (R2 = EtO) to give R12NCR(CN)C(OEt):CH2. All these products could be hydrolyzed to give mono- or diketones.

IT **128407-39-6P**
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and hydrolysis of)

RN 128407-39-6 HCAPLUS
CN 1-Pyrrolidineacetonitrile, α-[1-(methylthio)-3-phenyl-3-(1-pyrrolidinyl)-2-propenyl]-α-phenyl- (9CI) (CA INDEX NAME)



L15 ANSWER 10 OF 12 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1982:217316 HCAPLUS
DOCUMENT NUMBER: 96:217316
TITLE: Nucleophilic attack on olefins initiated by dimethyl(methylthio)sulfonium fluoroborate (DMTSF). Azasulfenylation



I

AB Reaction of the enamines RR1NCH:CHR2 (NRR1 = morpholino, R2 = Me, Et, Ph) with dimethylsuccinimidosulfonium fluorosulfate gave 42-94% RR1NCH:CR2S+Me2 FSO3- and 5-28% I (R = Me, Et). Alcoholysis of I gave the salts (R3O)2CHCHR2N+HRR1 FSO3- (R3 = Me, Et) which were deprotonated to (R3O)2CHCHR2NRR1.

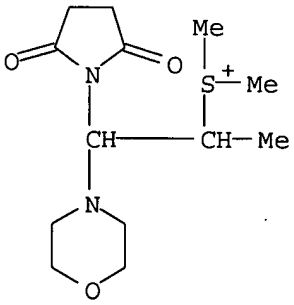
IT **75199-59-6P 75199-61-0P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of)

RN 75199-59-6 HCAPLUS

CN Sulfonium, [2-(2,5-dioxo-1-pyrrolidinyl)-1-methyl-2-(4-morpholinyl)ethyl]dimethyl-, (E)-, fluorosulfate (9CI) (CA INDEX NAME)

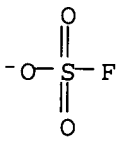
CM 1

CRN 75199-58-5
CMF C13 H23 N2 O3 S



CM 2

CRN 15181-47-2
CMF F O3 S

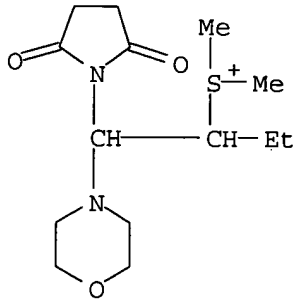


RN 75199-61-0 HCAPLUS

CN Sulfonium, [1-[(2,5-dioxo-1-pyrrolidinyl)(4-morpholinyl)methyl]propyl]dimethyl-, fluorosulfate (9CI) (CA INDEX NAME)

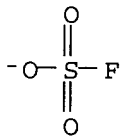
CM 1

CRN 75199-60-9
CMF C14 H25 N2 O3 S

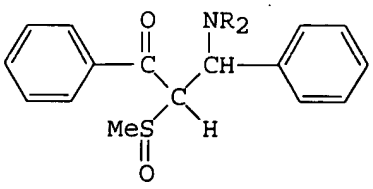


CM 2

CRN 15181-47-2
CMF F O3 S



L15 ANSWER 12 OF 12 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1979:574952 HCAPLUS
DOCUMENT NUMBER: 91:174952
TITLE: Thermolysis of Mannich bases from β-oxo sulfoxides, benzaldehyde and secondary amines
AUTHOR(S): Boehme, Horst; Clement, Bernd
CORPORATE SOURCE: Pharm.-Chem. Inst., Philipps-Univ., Marburg, 355, Fed. Rep. Ger.
SOURCE: Archiv der Pharmazie (Weinheim, Germany) (1979), 312(6), 531-4
CODEN: ARPMAS; ISSN: 0365-6233
DOCUMENT TYPE: Journal
LANGUAGE: German
GI



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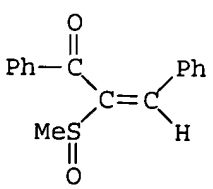


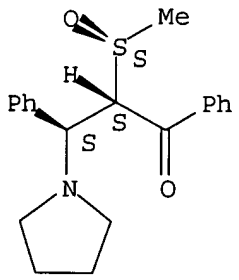
II

AB Stable Mannich bases I [R = Me, R2 = (CH2)4, CH2CH2OCH2CH2] were obtained as mixts. of 4 diastereoisomeric forms, stipulated by the 3 chiral centers, by condensation of PhCOCH2S(O)Me with PhCHO and HNR2. Amine elimination occurred on heating I (R = Me) >180° to give a single (E) diastereomer of the propenone II.

IT **71679-37-3P 71698-80-1P 71698-81-2P 71698-84-5P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of)

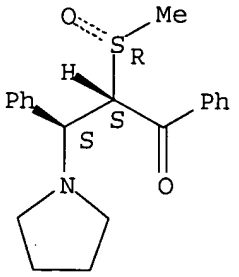
RN 71679-37-3 HCAPLUS
CN 1-Propanone, 2-(methylsulfinyl)-1,3-diphenyl-3-(1-pyrrolidinyl)-, [2R*(R*),3R*]- (9CI) (CA INDEX NAME)

Relative stereochemistry.



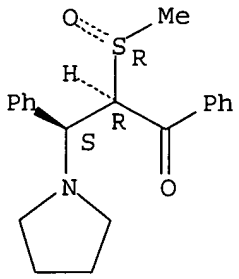
RN 71698-80-1 HCAPLUS
CN 1-Propanone, 2-(methylsulfinyl)-1,3-diphenyl-3-(1-pyrrolidinyl)-, [2R*(S*),3R*]- (9CI) (CA INDEX NAME)

Relative stereochemistry.



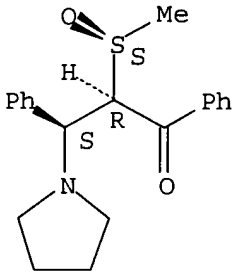
RN 71698-81-2 HCAPLUS
CN 1-Propanone, 2-(methylsulfinyl)-1,3-diphenyl-3-(1-pyrrolidinyl)-, [2R*(R*),3S*]- (9CI) (CA INDEX NAME)

Relative stereochemistry.



RN 71698-84-5 HCAPLUS
CN 1-Propanone, 2-(methylsulfinyl)-1,3-diphenyl-3-(1-pyrrolidinyl)-, [2R*(S*),3S*]- (9CI) (CA INDEX NAME)

Relative stereochemistry.



=> d l16 ibib abs hitstr tot

L16 ANSWER 1 OF 20 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 2005:1259355 HCAPLUS
DOCUMENT NUMBER: 144:22820
TITLE: Novel 4-oxoquinoline compounds and use thereof as HIV integrase inhibitors
INVENTOR(S): Satoh, Motohide; Matsuda, Takashi; Okuda, Satoshi; Kawakami, Hiroshi; Aramaki, Hisateru; Shinkai, Hisashi; Matsuzaki, Yuji; Watanabe, Wataru; Yamataka, Kazunobu; Kiyonari, Shinichi; Wamaki, Shuichi; Takahashi, Mitsuru; Yamada, Naohito; Nagao, Akemi
PATENT ASSIGNEE(S): Japan Tobacco Inc., Japan
SOURCE: PCT Int. Appl., 193 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2005113509	A1	20051201	WO 2005-JP9718	20050520

W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KP, KR, KZ,

LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW

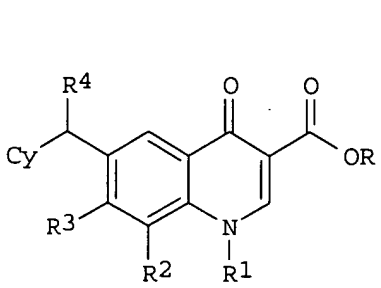
RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG

US 2006019906 A1 20060126 US 2005-133470 20050520

PRIORITY APPLN. INFO.: JP 2004-151034 A 20040520

OTHER SOURCE(S): MARPAT 144:22820

GI



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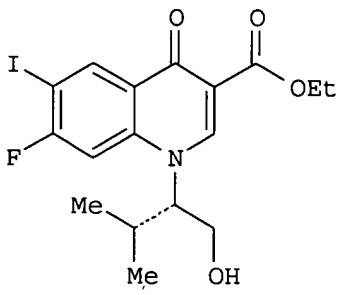
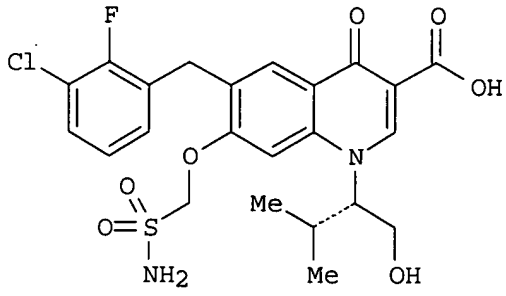


II



III

AB The 4-oxoquinoline compds. I, having an anti-HIV activity, and particularly an integrase inhibitory activity, are provided. Claims cover compds. I and their pharmaceutically acceptable salts, wherein: Cy = certain Ph groups substituted by combinations of Cl, F, and/or CF3, and also optionally with OH, OSO3H, or a uronic acid pyranoside; R = H or a uronic acid pyranoside; R1 is α-substituted β-hydroxyethyl or a uronic acid pyranoside thereof; R2 = H, OH, or certain OH derivs.; R3 = H, Et, OMe, OH, various OH derivs., certain saturated 5- and 6-membered heterocyclic amino groups, various OH and NH2 derivs.; R2R1 may form OCH2CHR5; R4 = H or OH; R5 = alkyl or hydroxyalkyl; with 7 addnl. provisos, including some specified names. The invention also relates to pharmaceutical compns. containing I or salts and pharmaceutically acceptable carriers; to integrase inhibitors, antiviral agents, anti-HIV agents, and the like, which contain I or their salts as active ingredients; to anti-HIV compns. containing I or salts and one or more other kinds of anti-HIV substances as active ingredients; to anti-HIV agents containing I or salts as

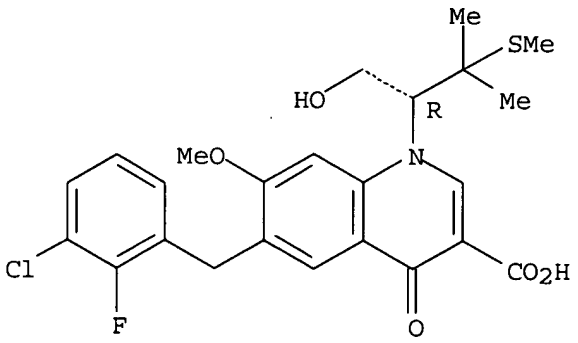
active ingredients, which are used for multiple-drug therapy with other anti-HIV agents; and the like. Over 100 compds. I are either listed or described in preparative and reference examples, with the listed compds. being claimed by name. For example, the intermediate quinoline II was prepared from 2,4-difluoro-5-iodobenzoic acid, Et 3-(dimethylamino)acrylate, and (S)-(+)-valinol. II underwent a sequence of O-protection as the Me carbonate, Pd-Zn-mediated benzylation at iodine, various deprotections and reprotections, hydroxydefluorination, etherification of the added hydroxy group, and final deprotection, to give invention compound III. This compound inhibited recombinant HIV integrase in vitro with an IC50 value of 0.0066 μM.

IT **870648-23-0P**, 6-(3-Chloro-2-fluorobenzyl)-1-[(1R)-1-(hydroxymethyl)-2-methyl-2-(methylthio)propyl]-7-methoxy-4-oxo-1,4-dihydroquinoline-3-carboxylic acid **870648-24-1P**, 6-(3-Chloro-2-fluorobenzyl)-1-[(1R)-1-(hydroxymethyl)-2-mesyl-2-methylpropyl]-7-methoxy-4-oxo-1,4-dihydroquinoline-3-carboxylic acid **870648-27-4P**, 6-(3-Chloro-2-fluorobenzyl)-1-[(1R)-1-(hydroxymethyl)-2-methyl-2-(methylthio)propyl]-4-oxo-1,4-dihydroquinoline-3-carboxylic acid **870648-28-5P**, 6-(3-Chloro-2-fluorobenzyl)-1-[(1R)-1-(hydroxymethyl)-2-mesyl-2-methylpropyl]-4-oxo-1,4-dihydroquinoline-3-carboxylic acid
RL: PAC (Pharmacological activity); SPN (Synthetic preparation); THU (Therapeutic use); BIOL (Biological study); PREP (Preparation); USES (Uses)
(drug candidate; preparation of novel oxoquinoline compds. as HIV integrase inhibitors)

RN 870648-23-0 HCAPLUS

CN 3-Quinolinecarboxylic acid, 6-[(3-chloro-2-fluorophenyl)methyl]-1,4-dihydro-1-[(1R)-1-(hydroxymethyl)-2-methyl-2-(methylthio)propyl]-7-methoxy-4-oxo- (9CI) (CA INDEX NAME)

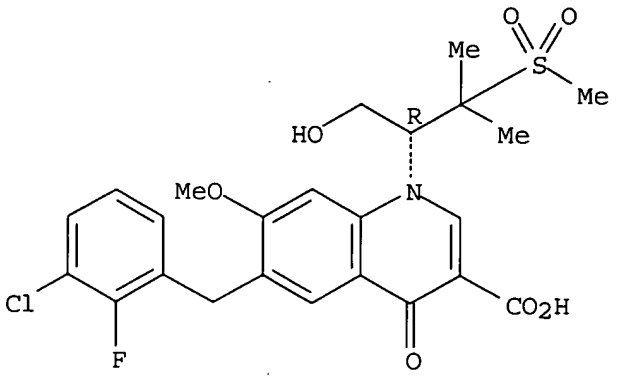
Absolute stereochemistry.



RN 870648-24-1 HCAPLUS

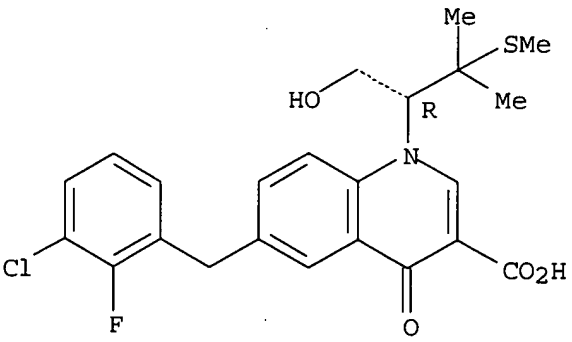
CN 3-Quinolinecarboxylic acid, 6-[(3-chloro-2-fluorophenyl)methyl]-1,4-dihydro-1-[(1R)-1-(hydroxymethyl)-2-methyl-2-(methylsulfonyl)propyl]-7-methoxy-4-oxo- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



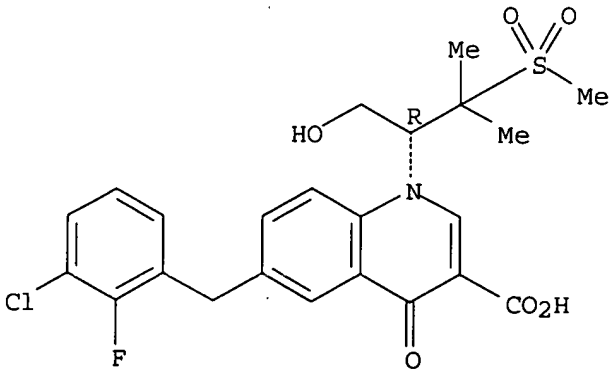
RN 870648-27-4 HCAPLUS
CN 3-Quinolinecarboxylic acid, 6-[(3-chloro-2-fluorophenyl)methyl]-1,4-dihydro-1-[(1R)-1-(hydroxymethyl)-2-methyl-2-(methylthio)propyl]-4-oxo- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



RN 870648-28-5 HCAPLUS
CN 3-Quinolinecarboxylic acid, 6-[(3-chloro-2-fluorophenyl)methyl]-1,4-dihydro-1-[(1R)-1-(hydroxymethyl)-2-methyl-2-(methylsulfonyl)propyl]-4-oxo- (9CI) (CA INDEX NAME)

Absolute stereochemistry.

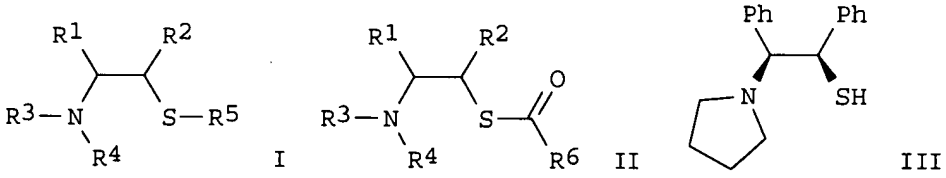


REFERENCE COUNT: 2 THERE ARE 2 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L16 ANSWER 2 OF 20 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 2005:354977 HCAPLUS
DOCUMENT NUMBER: 142:463603
TITLE: Aminoethanethiol derivatives as highly efficient chiral ligands in asymmetric reactions, especially in enantioselective nucleophilic addition of carbonyls with alkylmetals
INVENTOR(S): Yang, Denggui; Liu, Ta; Chen, Nanguang
PATENT ASSIGNEE(S): Haimen Huiju Pharmaceutical Co., Ltd., Peop. Rep. China
SOURCE: Faming Zhuanli Shenqing Gongkai Shuomingshu, 9 pp.
CODEN: CNXXEV
DOCUMENT TYPE: Patent
LANGUAGE: Chinese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
CN 1434034	A	20030806	CN 2001-143059	20011207

PRIORITY APPLN. INFO.: CN 2001-143059 20011207
OTHER SOURCE(S): CASREACT 142:463603
GI

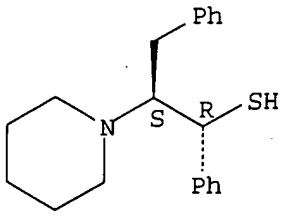


AB The invention relates to aminoethanethiol derivs. I and II [wherein R1, R2 = alkyl or aryl; R3, R4 = alkyl; R5, R6 = H or alkyl; etc.] and their applications as chiral ligands in asym. reactions, especially in asym. reduction of aldehydes through their organometallic (Zn, Cu and Ti) complexes and in enantioselective nucleophilic addition of carbonyl compds. with alkylmetals. The remarkably high asym.-induction efficiency of the invented compds. were demonstrated by three examples such as III using addition reaction of benzaldehyde with diethylzinc as probe. As little as 0.02% (molar ratio of ligand to substrate) of the ligands were enough to achieve >99% ee.

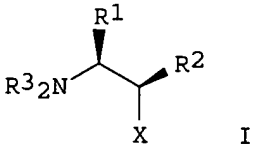
IT **851474-77-6**
RL: CAT (Catalyst use); USES (Uses)
(aminoethanethiol derivs. as highly efficient chiral ligands in asym. reactions)

RN 851474-77-6 HCAPLUS
CN 1-Piperidineethanethiol, α-phenyl-β-(phenylmethyl)-, (αR,βS)- (9CI) (CA INDEX NAME)

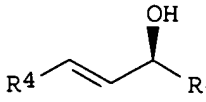
Absolute stereochemistry.



L16 ANSWER 3 OF 20 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 2005:130245 HCAPLUS
DOCUMENT NUMBER: 142:373291
TITLE: New β-amino thiols as efficient catalysts for highly enantioselective alkenylzinc addition to aldehydes
AUTHOR(S): Tseng, Shi-Liang; Yang, Teng-Kuei
CORPORATE SOURCE: Department of Chemistry, National Chung-Hsing University, Taichung, 40227, Peop. Rep. China
SOURCE: Tetrahedron: Asymmetry (2005), 16(4), 773-782
CODEN: TASYE3; ISSN: 0957-4166
PUBLISHER: Elsevier B.V.
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 142:373291
GI



I



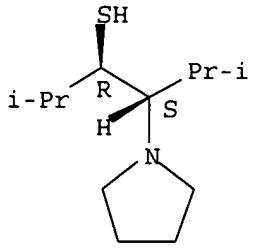
II

AB A series of new optically active β-amino thiols and thiol acetates I [X = HS, MeCOS; R1, R2 = Me2CH, Ph; R32 = (CH2)4, (CH2)5], prepared from the simple natural amino acid (S)-(-)-valine, were found to be effective catalysts for the enantioselective addition of alkenylzinc reagents R4CH:CHZnEt (R4 = n-Bu, Me3C, n-hexyl, Ph) to aldehydes R5CHO (R5 = cyclohexyl, Ph, 2-ClC6H4, 4-MeOC6H4, PhCH:CH) and thereby providing an efficient route to chiral (E)-allylic alcs. II with ees of up to >99%.

IT **757243-33-7P 757243-42-8P 757243-47-3P**
757243-55-3P 849599-88-8P 849599-91-3P
849599-94-6P
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)
(preparation of β-amino-substituted alcs., thiols and thiol acetates as chiral catalysts for enantioselective alkenylzinc addition to aldehydes)

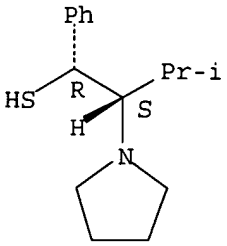
RN 757243-33-7 HCAPLUS
CN 1-Pyrrolidineethanethiol, α,β-bis(1-methylethyl)-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (+).



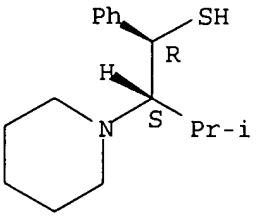
RN 757243-42-8 HCAPLUS
CN 1-Pyrrolidineethanethiol, β-(1-methylethyl)-α-phenyl-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



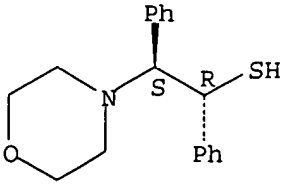
RN 757243-47-3 HCAPLUS
CN 1-Piperidineethanethiol, β-(1-methylethyl)-α-phenyl-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



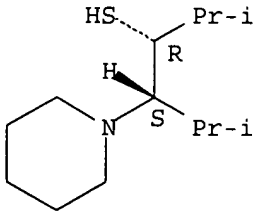
RN 757243-55-3 HCAPLUS
CN 4-Morpholineethanethiol, α,β-diphenyl-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



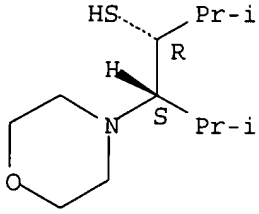
RN 849599-88-8 HCAPLUS
CN 1-Piperidineethanethiol, α,β-bis(1-methylethyl)-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



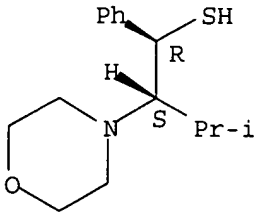
RN 849599-91-3 HCAPLUS
CN 4-Morpholineethanethiol, α,β-bis(1-methylethyl)-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



RN 849599-94-6 HCAPLUS
CN 4-Morpholineethanethiol, β-(1-methylethyl)-α-phenyl-, (αR,βS)- (9CI) (CA INDEX NAME)

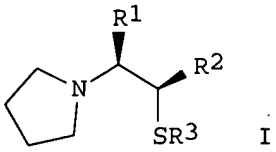
Absolute stereochemistry. Rotation (-).



REFERENCE COUNT: 28 THERE ARE 28 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L16 ANSWER 4 OF 20 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 2004:920913 HCAPLUS
DOCUMENT NUMBER: 142:74307
TITLE: The application of chiral amino thiols as catalysts in the enantioselective addition of diethylzinc to aldehydes
AUTHOR(S): Tseng, Shi-Liang; Yang, Teng-Kuei

CORPORATE SOURCE: Department of Chemistry, National Chung-Hsing University, Taichung, 40227, Taiwan
SOURCE: Tetrahedron: Asymmetry (2004), 15(21), 3375-3380
CODEN: TASYE3; ISSN: 0957-4166
PUBLISHER: Elsevier B.V.
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 142:74307
GI



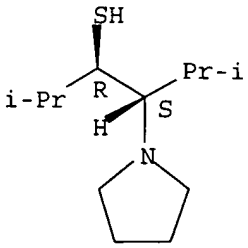
I

AB Starting from (S)-(-)-valine, a series of new chiral amino thiol and corresponding thioacetate ligands I (R1, R2 = Me2CH, Ph; R3 = H, MeCO) was prepared in an efficient manner and applied in the asym. diethylzinc addition to aldehydes R4CHO (R4 = Ph, 2-MeOC6H4, 2-naphthyl, n-octyl, etc.) to afford alcs. (R)-R4CH(OH)Et with excellent enantioselectivity (up to 99% ee) and with a catalytic loading as little as 0.02 mol % [for the amino thiol I (R1 = R2 = Ph; R3 = H)].

IT **757243-33-7P 757243-42-8P**
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)
(preparation of chiral amino thiols and their use as catalysts in enantioselective addition of diethylzinc to aldehydes)

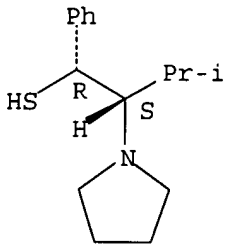
RN 757243-33-7 HCAPLUS
CN 1-Pyrrolidineethanethiol, α,β-bis(1-methylethyl)-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (+).



RN 757243-42-8 HCAPLUS
CN 1-Pyrrolidineethanethiol, β-(1-methylethyl)-α-phenyl-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).

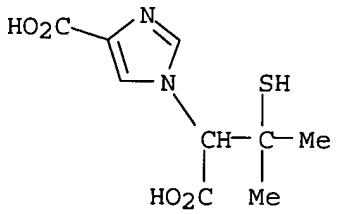


REFERENCE COUNT: 28 THERE ARE 28 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L16 ANSWER 5 OF 20 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 2004:763358 HCAPLUS
DOCUMENT NUMBER: 142:279556
TITLE: The molecular structure of penicillin
AUTHOR(S): Bentley, Ronald
CORPORATE SOURCE: Department of Biological Sciences, University of Pittsburgh, Pittsburgh, PA, 15260, USA
SOURCE: Journal of Chemical Education (2004), 81(10), 1462-1470
CODEN: JCEDA8; ISSN: 0021-9584
PUBLISHER: Journal of Chemical Education, Dept. of Chemistry
DOCUMENT TYPE: Journal
LANGUAGE: English

AB An overview of the observations that constitute a structure proof for penicillin, specifically aimed at the general student population is presented. The chemical methods used in the penicillin work were those of the "golden age" of organic chemical and penicillin may be regarded as the last of the major natural products to have been so investigated. M.ps. and b.ps. were criteria of purity and a crucial tool was microanal. leading to empirical formulas. For the rest, reliance was placed on chemical analogy and intuition, and on chemical synthesis. While limited use was made of column chromatog., paper and gas chromatog. were not available. Some very helpful information was provided by physicochem. methods, particularly potentiometric titration and IR spectroscopy. However, even to obtain a UV spectrum in those days required a special laboratory While the structure was determined, the overall goal of a reliable chemical synthesis was not. However, the use of specially selected fungal strains and of modern methods of bulk fermentation soon made penicillin available in quantities unimaginable to those who had worked with small quantities of the precious material. By careful standardization of conditions, and most importantly by extensive use of counter-current distribution for purification, they obtained a very small quantity of synthetic penicillin. However, it was not until 1957 that rational syntheses of penicillin became possible.

IT **847156-38-1DP**, derivs.
RL: SPN (Synthetic preparation); PREP (Preparation)
(rearrangement and degradation product of penicillin)
RN 847156-38-1 HCAPLUS
CN 1H-Imidazole-1-acetic acid, 4-carboxy-α-(1-mercapto-1-methylethyl)- (9CI) (CA INDEX NAME)



REFERENCE COUNT: 18 THERE ARE 18 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L16 ANSWER 6 OF 20 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 2004:759870 HCAPLUS
DOCUMENT NUMBER: 141:277501
TITLE: Preparation of 2-aminoethanethiol compounds as efficient catalysts for asymmetric addition reaction
INVENTOR(S): Yang, Teng-Kuei; Tseng, Shi-Liang; Liu, To; Chen, Nan-Kuang
PATENT ASSIGNEE(S): Taiwan
SOURCE: U.S. Pat. Appl. Publ., 15 pp., Cont.-in-part of U.S. Pat. Appl. 2003 153,781.
CODEN: USXXCO
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 2
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 2004181057	A1	20040916	US 2004-807710	20040323
US 20031537 81	A1	20030814	US 2002-39557	20020108
US 6861536	B2	20050301		

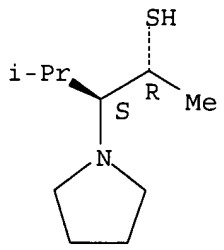
PRIORITY APPLN. INFO.: US 2002-39557 A2 20020108
OTHER SOURCE(S): MARPAT 141:277501
AB The present invention discloses aminothiol compds. having a general formula R3R4NCH(R1)CH(R2)SR5 (wherein R1-R4 = aryl, C1-9 alkyl; or R3, R4 and N form a three- to eight-membered heterocycle; R5 = H, C1-6 alkyl). Such compds. can perform as superior catalysts for the synthesis of chiral secondary alcs. by asym. addition reaction of organic metal compds. such organozinc compound and aldehyde. According to the present invention, the aminothiol compds. are needed only less than 0.02% based on main reactants to obtain enantioselectivity higher than 98% enantiomeric excess, whereby the asym. reactions can become very economic. Thus, cycloalkylation of (2R,3S)-3-amino-4-methylpentan-2-ol by 1,4-dibromobutane in the presence of Na2CO3 in MeCN under refluxing for 12 h gave (2R,3S)-4-methyl-3-(1-pyrrolidinyl)pentan-2-ol which was treated with MeSO2Cl and Et3N in CH2Cl2 for 2 h at 0° for 2 h, concentrated, and reacted with thioacetic acid in benzene at room temperature for 12 h to give 20% (2R,3S)-4-methyl-3-(1-pyrrolidinyl)-2-thioacetylpentane (I) and 40% (3R,4S)-2-methyl-4-(1-pyrrolidinyl)-3-thioacetylpentane (II). I or II was reduced by LiAlH4 in Et2O at 0° for 1 h to give (2R,3S)-4-methyl-3-(1-pyrrolidinyl)pentane-2-thiol or (3R,4S)-2-methyl-4-(1-pyrrolidinyl)pentane-3-thiol (III) in 80% yield. Asym. addition reaction of benzaldehyde with Et2Zn in toluene in the presence of 0.05 mequiv. (equivalence concentration)
III
at -20° for 12 h gave (R)-2-phenylpropanol (99.6% ee). Chiral (R)-1-phenyl-2-alken-1-ols were also prepared from butylacetylene and

hexylacetylene by monohydroboration of alkynes with BH3.SMe2 and transmetalation of boron to zinc with diethylzinc and asym. addition reaction with benzaldehyde or derivs. using the aminothiol catalysts.

IT **757242-87-8P**, (2R,3S)-4-Methyl-3-(1-pyrrolidinyl)pentane-2-thiol **757242-90-3P**, (3R,4S)-2-Methyl-4-(1-pyrrolidinyl)pentane-3-thiol **757243-14-4P**, (3S,4R)-2-Methyl-3-(1-pyrrolidinyl)octane-4-thiol **757243-19-9P**, (3R,4S)-2-Methyl-4-(1-pyrrolidinyl) octane-3-thiol **757243-33-7P**, (3R,4S)-2,5-Dimethyl-4-(1-pyrrolidinyl)hexane-3-thiol **757243-42-8P**, (1R,2S)-3-Methyl-1-phenyl-2-(1-pyrrolidinyl)butane-1-thiol **757243-47-3P**, (1R,2S)-3-Methyl-1-phenyl-2-piperidin-1-ylbutane-1-thiol **757243-55-3P**, (1R,2S)-1,2-Diphenyl-2-morpholin-4-ylethane-1-thiol
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)
(catalyst; preparation of 2-aminoethanethiol compds. as catalysts for asym. addition reaction of organic metal compound with aldehydes)

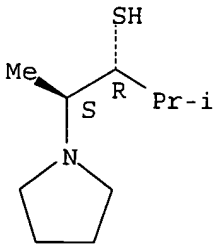
RN 757242-87-8 HCAPLUS
CN 1-Pyrrolidineethanethiol, α-methyl-β-(1-methylethyl)-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (+).



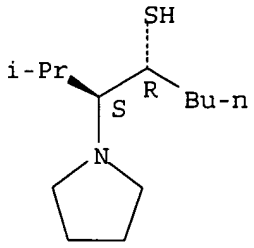
RN 757242-90-3 HCAPLUS
CN 1-Pyrrolidineethanethiol, β-methyl-α-(1-methylethyl)-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.



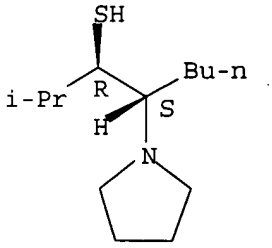
RN 757243-14-4 HCAPLUS
CN 1-Pyrrolidineethanethiol, α-butyl-β-(1-methylethyl)-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (+).



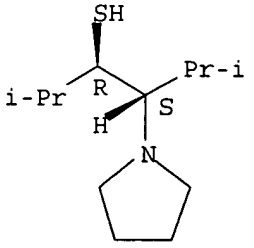
RN 757243-19-9 HCAPLUS
CN 1-Pyrrolidineethanethiol, β-butyl-α-(1-methylethyl)-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (+).



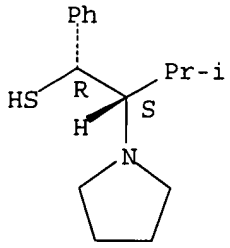
RN 757243-33-7 HCAPLUS
CN 1-Pyrrolidineethanethiol, α,β-bis(1-methylethyl)-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (+).



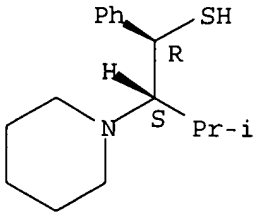
RN 757243-42-8 HCAPLUS
CN 1-Pyrrolidineethanethiol, β-(1-methylethyl)-α-phenyl-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



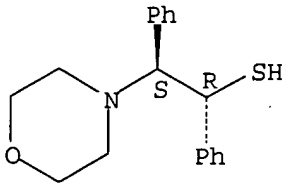
RN 757243-47-3 HCAPLUS
CN 1-Piperidineethanethiol, β-(1-methylethyl)-α-phenyl-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).



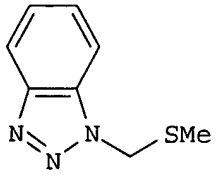
RN 757243-55-3 HCAPLUS
CN 4-Morpholineethanethiol, α,β-diphenyl-, (αR,βS)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).

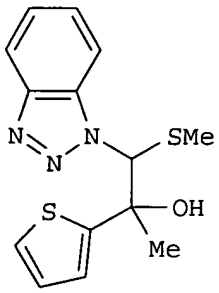


L16 ANSWER 7 OF 20 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 2004:384687 HCAPLUS
DOCUMENT NUMBER: 141:140365
TITLE: Benzotriazolyl-Mediated 1,2-Shifts of Electron-Rich Heterocycles
AUTHOR(S): Katritzky, Alan R.; Bobrov, Sergey; Khashab, Niveen; Kirichenko, Kostyantyn
CORPORATE SOURCE: Center for Heterocyclic Compounds, University of Florida, Gainesville, FL, 32611-7200, USA
SOURCE: Journal of Organic Chemistry (2004), 69(12), 4269-4271 CODEN: JOCEAH; ISSN: 0022-3263
PUBLISHER: American Chemical Society
DOCUMENT TYPE: Journal
LANGUAGE: English
OTHER SOURCE(S): CASREACT 141:140365

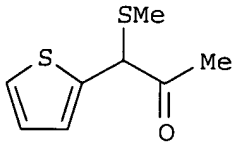
GI



I



II



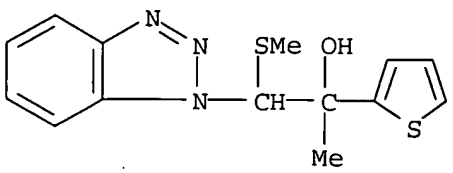
III

AB The anion formed from the lithiation of 1-[(methylthio)methyl]-1H-benzotriazole (I) with n-BuLi adds to heteroaryl ketones to give 2-benzotriazolyl alcs., e.g., II. Thermolysis of the alcs. in the presence of zinc bromide induces a 1,2-shift of heteroarom. groups to form ketones, e.g., III. By contrast, in the rearrangement of 2-benzotriazolyl heteroaryl Ph alcs., migration of the Ph group rather than the corresponding heteroarom. groups occurred.

IT **725265-37-2P 725265-38-3P 725265-39-4P**
725265-40-7P 725265-41-8P 725265-42-9P
725265-43-0P 725265-44-1P 725265-45-2P
725265-47-4P 725265-48-5P 725265-49-6P
725265-60-1P 725265-61-2P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation of α-(methylthio)ketones via addition of (methylthio)methylbenzotriazole to ketones followed by 1,2-shift)

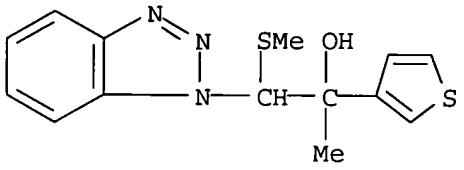
RN 725265-37-2 HCAPLUS

CN 1H-Benzotriazole-1-ethanol, α-methyl-β-(methylthio)-α-2-thienyl- (9CI) (CA INDEX NAME)

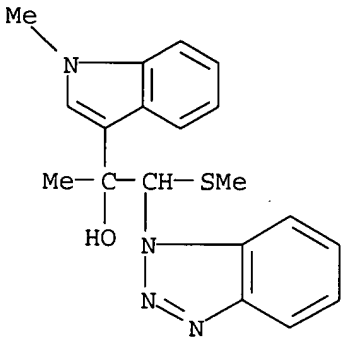


RN 725265-38-3 HCAPLUS

CN 1H-Benzotriazole-1-ethanol, α-methyl-β-(methylthio)-α-3-thienyl- (9CI) (CA INDEX NAME)

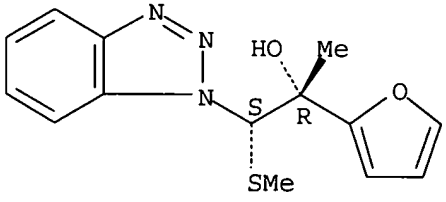


RN 725265-39-4 HCAPLUS
CN 1H-Benzotriazole-1-ethanol, α-methyl-α-(1-methyl-1H-indol-3-yl)-β-(methylthio)- (9CI) (CA INDEX NAME)

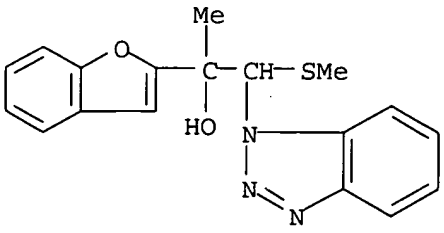


RN 725265-40-7 HCAPLUS
CN 1H-Benzotriazole-1-ethanol, α-2-furanyl-α-methyl-β-(methylthio)-, (αR,βS)-rel- (9CI) (CA INDEX NAME)

Relative stereochemistry.

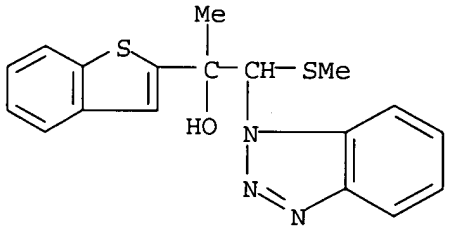


RN 725265-41-8 HCAPLUS
CN 1H-Benzotriazole-1-ethanol, α-2-benzofuranyl-α-methyl-β-(methylthio)- (9CI) (CA INDEX NAME)



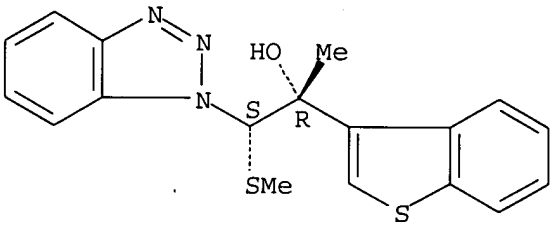
RN 725265-42-9 HCAPLUS
CN 1H-Benzotriazole-1-ethanol, α-benzo[b]thien-2-yl-α-methyl-

β-(methylthio)- (9CI) (CA INDEX NAME)

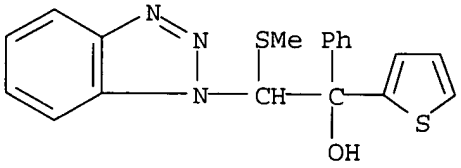


RN 725265-43-0 HCAPLUS
CN 1H-Benzotriazole-1-ethanol, α-benzo[b]thien-3-yl-α-methyl-β-(methylthio)-, (αR,βS)-rel- (9CI) (CA INDEX NAME)

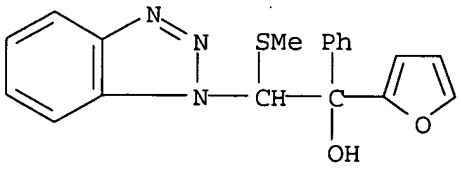
Relative stereochemistry.



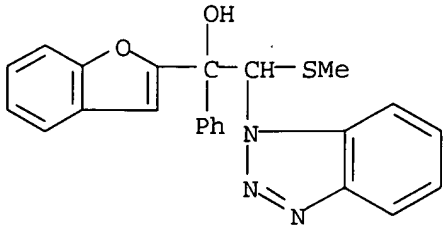
RN 725265-44-1 HCAPLUS
CN 1H-Benzotriazole-1-ethanol, β-(methylthio)-α-phenyl-α-2-thienyl- (9CI) (CA INDEX NAME)



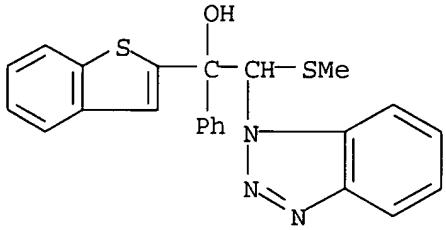
RN 725265-45-2 HCAPLUS
CN 1H-Benzotriazole-1-ethanol, α-2-furanyl-β-(methylthio)-α-phenyl- (9CI) (CA INDEX NAME)



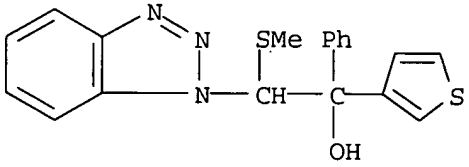
RN 725265-47-4 HCAPLUS
CN 1H-Benzotriazole-1-ethanol, α-2-benzofuranyl-β-(methylthio)-α-phenyl- (9CI) (CA INDEX NAME)



RN 725265-48-5 HCAPLUS
CN 1H-Benzotriazole-1-ethanol, α-benzo[b]thien-2-yl-β-(methylthio)-α-phenyl- (9CI) (CA INDEX NAME)

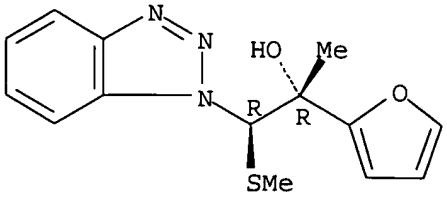


RN 725265-49-6 HCAPLUS
CN 1H-Benzotriazole-1-ethanol, β-(methylthio)-α-phenyl-α-3-thienyl- (9CI) (CA INDEX NAME)



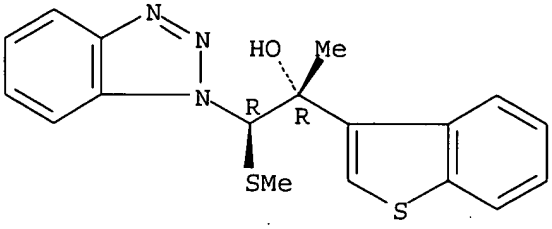
RN 725265-60-1 HCAPLUS
CN 1H-Benzotriazole-1-ethanol, α-2-furanyl-α-methyl-β-(methylthio)-, (αR,βR)-rel- (9CI) (CA INDEX NAME)

Relative stereochemistry.

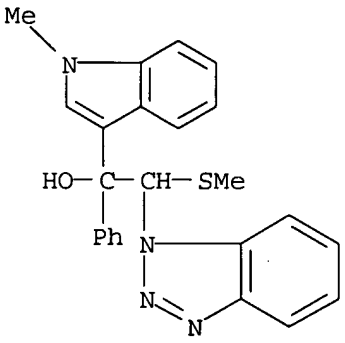


RN 725265-61-2 HCAPLUS
CN 1H-Benzotriazole-1-ethanol, α-benzo[b]thien-3-yl-α-methyl-β-(methylthio)-, (αR,βR)-rel- (9CI) (CA INDEX NAME)

Relative stereochemistry.



IT **725265-46-3P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(preparation of α-(methylthio)ketones via addition of (methylthio)methylbenzotriazole to ketones followed by 1,2-shift)
RN 725265-46-3 HCAPLUS
CN 1H-Benzotriazole-1-ethanol, α-(1-methyl-1H-indol-3-yl)-β-(methylthio)-α-phenyl- (9CI) (CA INDEX NAME)



REFERENCE COUNT: 14 THERE ARE 14 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L16 ANSWER 8 OF 20 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 2004:34526 HCAPLUS
DOCUMENT NUMBER: 141:274075
TITLE: Bandunamide, a novel cyclopeptide from the Streptomyces griseovariabilis bandungensis
AUTHOR(S): Tian, Xing Shan; Xie, Shuang Da; Jiang, Xue Bing; Zhou, Xiao Mao; Yang, Li Mei; Xiao, Ding Jun
CORPORATE SOURCE: Guangdong Academy of Agricultural Sciences, Guangzhou, 510640, Peop. Rep. China
SOURCE: Chinese Chemical Letters (2003), 14(12), 1255-1258
CODEN: CCLEE7; ISSN: 1001-8417
PUBLISHER: Chinese Chemical Society
DOCUMENT TYPE: Journal
LANGUAGE: English
AB A new cyclic octapeptide, bandunamide, was isolated from the acetone exts. of Streptomyces griseovariabilis bandungensis. This cyclic octapeptide exhibits strong antimicrobial activity against Phytophthora drechsleri (IC50=15 ng/mL), Colletotrichum graminicola, (IC50=15.6 ng/mL), Pyricularia oryzae, (IC50=0.2 μg/mL), and Fusarium oxysporum f. sp. (IC50=100 μg/mL). The structure elucidation of bandunamide is herein reported.
IT **757955-06-9P**, Bandunamide

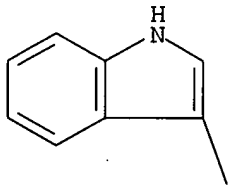
RL: BSU (Biological study, unclassified); NPO (Natural product occurrence); PAC (Pharmacological activity); PRP (Properties); PUR (Purification or recovery); BIOL (Biological study); OCCU (Occurrence); PREP (Preparation)
(isolation and characterization of bandunamide as a novel antimicrobial cyclopeptide from Streptomyces griseovariabilis bandungensis)

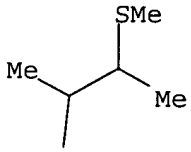
RN 757955-06-9 HCAPLUS

CN Cyclo[alanyl-N-methyl-β-(methylthio)tryptophyl-N,3-dimethyl-4-(methylthio)norvalylserylalanyl-N-methyltryptophyl-N,3-dimethyl-4-(methylthio)norvalylseryl] (9CI) (CA INDEX NAME)

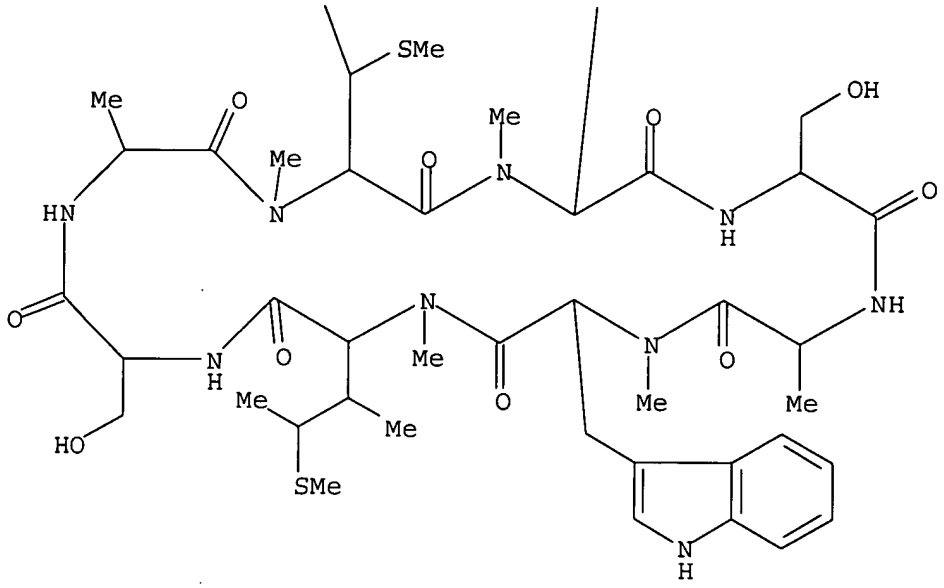
Currently available stereo shown.

PAGE 1-A





PAGE 2-A



REFERENCE COUNT: 6 THERE ARE 6 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L16 ANSWER 9 OF 20 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1964:447807 HCAPLUS
DOCUMENT NUMBER: 61:47807
ORIGINAL REFERENCE NO.: 61:8284a-b
TITLE: Preparation of quaternary ammonium betaine salts
INVENTOR(S): Klass, Donald L.
PATENT ASSIGNEE(S): Pure Oil Co.
SOURCE: 4 pp.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

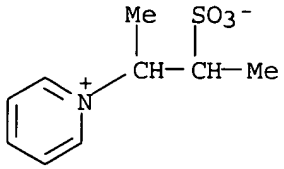
PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 3131189		19640428	US 1961-145464	19611016
PRIORITY APPLN. INFO.:			US	19611016

GI For diagram(s), see printed CA Issue.

AB Carbyl sulfate (I), prepared by the reaction of 2 moles SO3 and 1 mole ethylene, reacted with a tertiary amine to form betaines. Thus 1.5 g. pyridine (II) in 10 ml. ethylene dichloride was added to 3 g. I in 30 ml. ethylene dichloride (the reaction was exothermic), the liquid decanted from the precipitate, and the precipitate covered with petr. ether and cooled to give IIa (R = R1 = H), m. 250-5° (HCONMe2). I was also treated with the following to form betaines: quinoline, acridine, trimethylamine, and dimethylaniline (III). Also reported without details were: IIa (R = Ph, R1 = H); Et3NCHEtCH2SO3; IIa (R = R1 = Me); and PhNMe2CMe2CMe2SO3. These compds. are useful intermediates for the preparation of detergents. (Cf. U.S. 2,666,788, or Brit. 686,061.)

IT **859804-42-5**, Pyridinium, 1-(1-methyl-2-sulfopropyl)-, hydroxide, inner salt

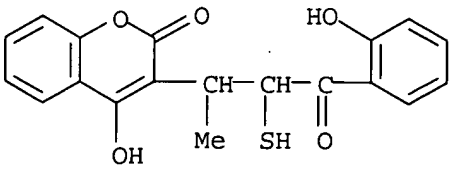
(preparation of)
RN 859804-42-5 HCAPLUS
CN Pyridinium, 1-(1-methyl-2-sulfopropyl)-, hydroxide, inner salt (7CI) (CA INDEX NAME)



L16 ANSWER 10 OF 20 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1959:7142 HCAPLUS
DOCUMENT NUMBER: 53:7142
ORIGINAL REFERENCE NO.: 53:1383g-h
TITLE: 1-(Salicylyl)-2-(4-hydroxy-3-coumarinyl)propyl alkyl thioethers
INVENTOR(S): Fucik, Karel
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
CS 86507		19570515	CS	

AB 1,1-Bis(4-Hydroxy-3-coumarinyl)ethyl methyl thioether (150 g.) added to 1500 ml. boiling 10% NaOH solution, the mixture boiled 1 hr., poured on ice, acidified with HCl to pH 2, the separated product let stand 4 hrs., washed with H2O, dried at 70°, and recrystd. from EtOH gave 125 g. title compound (I) (alkyl = Me), m. 154-5°. Similarly are obtained I (alkyl, m.p., and % yield given): Et, 158°, 85; allyl, 159°, 72; Pr, 144°, 75; iso-Pr, 146°, 79; Bu, 124-5°, 75; iso-Bu, 137°, 75; iso-Am, 114°, 73. Ultraviolet spectra of I (alkyl = Me and Et) are charted.
IT **859923-26-5**, Coumarin, 4-hydroxy-3-(2-mercapto-1-methyl-2-salicyloylethyl)-
(S-alkyl derivs.)
RN 859923-26-5 HCAPLUS
CN Coumarin, 4-hydroxy-3-(2-mercapto-1-methyl-2-salicyloylethyl)- (6CI) (CA INDEX NAME)



L16 ANSWER 11 OF 20 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1955:15989 HCAPLUS
DOCUMENT NUMBER: 49:15989

ORIGINAL REFERENCE NO.: 49:3165a-i,3166a-i,3167a-i,3168a-i,3169a-b
TITLE: Penillic acids and penillamines
AUTHOR(S): Cook, A. H.
CORPORATE SOURCE: Imperial Coll. Sci, London
SOURCE: Chem. of Penicillin (1949) 105-43
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
GI For diagram(s), see printed CA Issue.
AB The facile formation and isolation of penillic acids provided a pure derivative of penicillin for degradative work at an early stage in the study of the chemical of the penicillins. The optical activity of 0.5% 2-pentenylpenicillin Ba salt, activity 1200 units per mg., adjusted to pH 2-3 with NH_2SO_4, increased while standing for 5 h. at room temperature Centrifuging and extracting with Et_2O removed the levorotatory yellow-green pigment. The colorless dextrorotatory aqueous solution was extracted with BuOH and yielded 20% of 2-pentenylpenillic acid (I), m. 173° (decomposition), $[\alpha]_{5461}$ 600° (c 2%, H_2O), $[\alpha]_{D}^{16.5}$ 527° (±10), λmaximum 2380 A., E1cm1% 192, giving a blue-purple color with ninhydrin, a precipitate with phosphotungstic acid, $HgCl_2$, and $AgNO_3$, but no blue thiol reaction with $FeCl_3$, and decolorizing Br in H_2O. Treatment of I (0.3% in H_2O) with excess 5% $HgCl_2$ produced a white precipitate Suspension of the precipitate in H_2O, decomposition with H_2S and evaporation of the levorotatory solution over H_2SO_4 gave 2-pentenylpenillamine-HCl (II), $[\alpha]_{546120}$ -88° (c 1.2, H_2O), giving a blue thiol reaction with $FeCl_3$ but no amino N by Van Slyke procedure. With ninhydrin a fine red color was obtained but not the typical blue of amino acids. Br oxidation of I and II in H_2O yielded penicillaminic acid (III), $[\alpha]_{546120}$ -22° (c 1, H_2O). Similarly, benzylpenicillin was converted to benzylpenillic acid (IV), m. 189°, $[\alpha]_{D}^{1605}$ 500° (± 10), λmaximum 2393 A., E1cm1% 148.5, oxidized to benzylpenillamine-HCl, m. 169-70° (decomposition), $[\alpha]_D$ -65.1° (H_2O). The Ba salt of a penicillin obtained from strain 1248 was reduced over PtO_2 and the crude product, m. 190-9° (decomposition), was oxidized with $HgCl_2$ to give p-hydroxybenzylpenillic acid (V), m. 218°, $[\alpha]_{D}^{17.5}$ 478°, λmaximum 2780 A.; p-benzyloxy derivative, m. 186°. V was hydrolyzed by boiling with 10% HCl for 3 h. to p-$HOC_6H_4CH_2CO_2H$, m. 148°. Ba penicillin "IV" at pH 2.2 for 1 h. at 37° yielded penillic-"IV" acid, m. 176°, $[\alpha]_{D}^{22}$ 490°, λmaximum 2365 A., E1cm1% 197, identical with the product from the hydrolysis of crude NH_4 n-heptylpenicillinate; n-heptylpenillic acid, m. 171-1.5°, $[\alpha]_{D}^{24}$ 480°, λmaximum 2150 A., EM 3400. The structure of penillic acids follows almost automatically from that of penicilloic acid and the recognition that 2 acidic centers and a basic group are present with the consequence that the loss of H_2O involves the O of the amide side chain. Similarly, since penillamine is a thiol formed with loss of CO_2 from penillic acid, its constitution follows. The UV absorption of IV was difficult to reconcile with the proposed structure even after making allowance for possible migration of double bonds. The comparable isolated systems, N:C-CO_2H, C:CCO_2H, and C:CPh absorbed at 2100, 2250 and 2450-2550 A., resp. Although the imidazolecarboxylic acids absorbed in the same region as IV it was expected that as dihydroimidazoles they would absorb at a lower wave length and that the influence of the S atom was to be anticipated. Absorption measurements are recorded for 20 compds., in the substituted acrylic acid and imidazole-carboxylic acid series. Condensation of $PhCH_2C(:NH)$-NH_2 with

H2NCH2CH(NH2)CO2H.HBr in CHCl3 gave 2 forms of 2-benzylimidazoline-4-carboxylic acid, m. 302-4° (decomposition) and 210-11°. Both showed only end absorption. Some of the 20 compds. lost the absorption band on decarboxylation, as does IV, thus confirming the presence of the system C.C(CO2H):N. The difference of absorption spectrum of 2-pentenylisopenillic acid (VI) from that of Et 4-carbethoxy-2-benzylimidazole-1-acetate, m. 111-12°, is ascribed to the thiol grouping. The mechanism of the formation of penillic acids from penicillins has been compared to a similar effect due to H ions in acetylations by acid anhydrides and in the hydrolysis of Ac2O. The change has also been compared with the rearrangements of certain imino ethers, though the transformation is not closely comparable with any other known rearrangement reaction. Attempts to provide a model for the reaction led to efforts to synthesize the azolactone, OC.O.CPh: N.CHCH2NHCH2CO2H. Addition of 13.75 g. EtO2CCH2NH2.HCl in 75 mL. H2O to a suspension of 25 g. BzNHCNa(HCO)CO2Et in 80 mL. EtOH gave N-(β-carbethoxy-β-benzamidoethylidene)glycine Et ester, m. 114-15°, reduced in MeOH in the presence of Raney Ni catalyst to N-(β-carboxy-β-benzamidoethyl)glycine, m. 192-3°; Bz derivative, m. 194-5°; carbobenzyloxy derivative, m. 147-9°, partially (15%) converted by cold Ac2O to a crude azlactone giving a benzylamide, m. 185-6°. Since the catalytic removal of the PhCH2OCO group was not achieved the plan was abandoned. In another attempt the addition of 14 mL. H2O to a mixture of NCC(:NOH)CO2Et and 2.5 g. Hg-Al in 250 mL. of boiling Et2O in 1.5 h. gave 12 g. of crude NCCH(NH2)CO2Et, acylated to NCCH(NHCOCH2Ph)CO2Et, m. 129°. Treatment of the solution with 1.99N NaOH yielded NCCH(NHCOCH2Ph)-CO2Na, reduced over 30% Raney Ni in the presence of NH4OH to α-phenylacetamido-β-alanine (VII), m. 233-4°; β-N-benzoyl derivative (VIIa), m. 160-1°; formyl derivative (VIIb), m. 180-1° (decomposition); carbobenzyloxy derivative (VIIc), m. 126-7°. Though VIIa gave an azlactone, m. 178-80° (benzylamide, m. 220-1°), with Ac2O (but not with PBr3), VII, VIIb, and VIIc could not be so dehydrated. The difficulty of removing the PhCH2OCO group precluded the attainment of any true model for the penillic acid change. Attempts to reduce catalytically the Schiff bases from Ph-CH2NH2 or PhNH2 and Et benzylpenaldate or to condense the amines with Me α-phenylacetamido-β-chloropropionate were inconclusive. The phys. properties of penillic acids and penillamines are recorded in collected form. Observations relating to deuterium exchange in IV and deuteration in its formation process are discussed. Titrns. of IV as a dicarboxylic acid with a weakly basic group are best summarized in the now accepted structure. Further chemical reactions of the penillic acids are described. Refluxing I with a large excess of Raney Ni in MeOH gave CO2 and a decomposition product free of S and N. Hydrogenolysis of IV in aqueous NaHCO3 reduced over Raney Ni produced 2 new compds., m. 239-42° and 175-7°. Oxidation of IV with ammoniacal Ag2O gave a substance, m. 140-50°, closely related to benzylpenillamine (VIII). I and IV readily lost S in the presence of Na2PbO2. Electrometric Br titration of IV in 2N H2SO4 consumed 6 equivs. of Br with probable formation of a sulfonic acid. IV oxidized with iodine slower than did simple thiazolidines. Digestion with hot N HNO3 apparently converted I to III. The Na salt of IV gave no precipitate or coloration with FeCl3 or CuSO4, no reduction of AgNO3 or Hg(OAc)2, or of cold Tollen reagent or boiling Fehling solution The nitroprusside test was neg. in strong alkali, but gave a faint persistent pink with KCN instead of NaOH or at pH 6.8. The ferricyanide thiol test was neg. in aqueous NaHCO3, but pos. at pH 6.8. IV was not converted to an aldehyde with HgCl2, gave no amino test by Van Slyke procedure but showed a strong azide reaction. When distilled with Zn dust, IV yielded a base,

probably 1-methyl-2-benzyl-4,5-dihydroimidazole. No biol. reactivation was observed on irradiating the penillic acids with sunlight or Hg are light alone or in the presence of iodine, Br, BzO2H, or, on treating with BF3 in ether, with various acids or PhNCO. IV had no stimulating action on the production of penicillin by Penicillium notatum. By keeping in 0.2N Ba(OH)2 at 37° overnight, I was converted into VI, m. 195-6° (decomposition). Similar treatment of IV for 3 days gave benzyl-isopenillic acid (IX), m. 174° (decomposition), transformed by treatment with HgCl2 in MeOH to VIII. Reaction of IV with 5 equivs. of HgCl2 in MeOH at 23° showed a rapid fall of [α]D (483 to 125° in 30 min.) followed by a slow fall (-60°. after 46 h.), the penillic acid absorption being replaced by strong end absorption, indicating successive reactions of penillic acid. Di-Me benzylpenillate (X) underwent a similar stepwise reaction. Refluxing 100 mg. IV in 60 mL. MeOH for 18-20 h. to zero rotation gave IX, [α]D -30° (c 2.5, MeOH), showing no HS group in alkali but apparent in 0.5N HNO3. VIII.HCl, m. 174°, [α]D -70.7° (in H2O) resisted treatment with hot 0.1N H2SO4 and could not be oxidized by Br in H2O to III. VIII gave the usual thiol color reactions, a faint ninhydrin reaction and an orange-red color with diazotized p-H2NC6H4SO3H. VIII was unchanged by refluxing with 0.1N H2SO4 for 2.5 h. but consumed 6 g.-atoms Br on titration with aqueous Br. The lowering of the 2375 A. band of VIII at pH 11.6 indicated formation of benzylpenicilloic acid rather than of IX. Rearrang ement of X by boiling in xylene gave di-Me benzyl-isopenillate (XI), m. 127-9°, [α]D -9.4° (c 1.4, MeOH), also formed by keeping X in aqueous AcOH. Methanolysis of 43 mg. XI by heating with 0.5 mL. MeOH (sealed tube) yielded 10 mg. of 4-carbomethoxy-2-benzylimidazole, m. 205-19°. The hydrogenolysis of XI or of IV, but not o penicillin, gave rise to the noncharacterized benzyldethio penillic acid, not formed by conversion of benzyldethiopenicillin under the usual conditions. Desulfurization of VIII with Raney Ni gave presumably α-(2-benzyl-1-imidazolyl)isovaleric acid (XII). Preparation of the 4,5-dihydro derivative, α-(2-benzyl-2-imidazolin-1-yl)isovaleric acid (XIIa), was undertaken to study the synthesis of XII and VIII. Condensation of 30 g. AcNHCH2CH2NH2 in 95% EtOH with 10 g. Me2CHCHBrCO2H yielded 9 g. of Me2CHCH(NHCH2CH2NHAc)CO2H, m. 214-16°; HCl salt, m. 254-6°; di-HCl salt, m. 213-15°. Addition of excess PhCH2CS2Na to 9.5 g. HCl salt in 20 mL. H2O containing 2 g. NaOH and acidification yielded 7.5 g. of Me2CHCH(NHCH2CH2NCSCH2Ph)CO2H, m. 197-9°, converted by refluxing for 46 h. to XIIa, m. 211-13°. Attempts to dehydrogenate XIIa to XII with Raney Ni in MeCH(OH)CH2OH, BzOEt, or PhCH:CHCO2Et were unsuccessful. Penillamine syntheses from 4-carboxy-5,5-dimethyl-2-acylamidomethylthiazolidines were successful only under carefully controlled conditions and with selected compds. A mixture of 100 mg. of DL-penicillamine-HCl (XIII) and 150 mg. of caproamidoacetal was warmed in 2N HCl for 1 min. and evaporated in vacuo over P2O5, yielding 4-carboxy-5,5-dimethyl-2-caproamidomethylthiazolidine-HCl (XIV), m. 201°. A suspension of 22.1 g. XIV in 190 mL. POCl3 and 5 g. of sirupy H3PO4 was concentrated to 50 mL. in vacuo, diluted with dioxane, taken up in cold aqueous NaHCO3 and filtered, yielding the insol. diketo piperazine, m. 185-6°. Extraction of the filtrate with BuOH gave a "decarboxyamylpenillic acid," oxidized by treatment in MeOH with 5% aqueous HgCl2 and decomposition of the precipitate with H2S to give DL-n-amylpenillamine-HCl, m. 170°, λmaximum 2180 A., E1cm.1% 230, identical with the natural material. Acetylation of 20 g. H2NCH2CH(OEt)2 with 23 g. PhCH2COCl in 200 mL. of ice-cold 5% aqueous NaOH yielded 21.7 g. of phenylacetamidoacetaldehyde di-Et acetal, m. 33-5°;

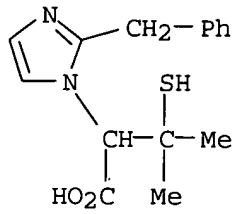
2,4-dinitrophenylhydrazone, m. 201-2° (decomposition). Condensation of 1.7 g. acetal with 1.0 g. XIII in 5 mL. MeOH for 5 min. gave 4-carboxy-5,5-dimethyl-2-(phenylacetamidomethyl)-thiazolidine-HCl, m. 193.5° (decomposition). Dehydration of 4 g. of HCl salt in 15 mL. POCl3 for 40 h., evaporation, solution in 200 mL. dioxane, stirring in 200 mL. of ice-cold aqueous NaHCO3 and filtration gave an insol. diketo piperazine derivative, m. 234-5°. Extraction of the filtrate with BuOH yielded a "decarboxybenzylpenillic acid," converted by treatment with HgCl2 and decomposition with H2S to DL-benzylpenillamine-HCl (XV), m. 173-4° (sic, vide infra), λmaximum 2150, E1cm.1% 350; picrate, m. 156-7°, identical with natural material. In an effort to improve on this synthesis removal of H2S from the corresponding thioamides was attempted. The addition of 3 mL. of H2NCH2CH(OEt)2 to 6.3 g. of PhCHCS2H in 60 mL. H2O containing 4 g. Na2CO3 and extraction with Et2O after 12 h. gave PhCH2CSNHCH2CH(OEt)2 (XVI), b0.07 155-8°; 2,4-(O2N)C6H3NHN:CHCH2NHCSCH2Ph, m. 194°. Refluxing a mixture of 1.2 g. XVI and 0.8 g. XIII in 10 mL. BuOH for 30 min. with copious evolution of H2S and precipitation with Et2O produced crude DL-decarboxybenzylpenillic acid (XVIa); this with HgCl2 gave a precipitate which was decomposed with H2S to crude XV, purified through the picrate, m. 159-60°. Similar use of dithiocaproic acid (XVI) and its Me ester as a route to amylpenillamine (XVII) was without success. XV was also synthesized by way of XVIa. Condensation of 1.48 g. XIII and 1.08 g. H2NCH2CH(OEt)2 (XVIII) in 16 mL. N HCl at 37° for 15 h. concentration, and recrystn. from a mixture of MeOH and AcOH containing a drop of concentrated HCl yielded 720 mg. of DL-4-carboxy-5,5-dimethyl-2-aminomethylthiazolidine-2HCl, m. 194° (decomposition). Addition of 1.3 mL. of 2N PhCH2CS2Na to 680 mg. of the di-HCl salt in 3.9 mL. 2N NaOH produced 300 mg. of DL-4-carboxy-5,5-dimethyl-2-phenylthioacetamidomethylthiazolidine-HCl, m. 188° (decomposition), converted by heating 270 mg. in 1.1 mL. quinoline at 130° under N to XVIa, m. 196°. XVIa (33 mg.) in 5 mL. H2O was heated with excess HgCl2 and after 30 min. the precipitate was centrifuged and washed. An aqueous suspension containing 0.15 mL. N HCl was decomposed with H2S. Evaporation of the supernatant liquid gave a sirup crystallizing to 34 mg. of XV, m. 193° (sic, vide supra), with 3 ionizable groups, pK 1.8, 7.0 and 10.5, evidently corresponding to acidic, basic, and thiol groups. When D and L-penicillamine-HCl (XIIIa, XIIIb) are condensed with caproamidoacetal (XIX) and similar compds., each penicillamine configuration should yield 2 geometrically isomeric thiazolidines. A mixture of 2.5 g. XIIIb and 3.1 g. XIX was warmed to 60° until the melt solidified. Crystallization from AcOH gave L-4-carboxy-5,5-dimethyl-2-caproamidomethyl-thiazolidine-HCl, m. 193-4° (decomposition), [α]D21 -82.3° (c 0.875, EtOH); after 10 min. at 50°, [α]D21 76.5°. Similarly, XIIIa gave the D-form, m. 193-4°, [α]D21 83.7° (c 0.239, EtOH); after 10 min. at 50°, [α]D25 75.3°. Each optically pure thiazolidine (1.5 g.) in 10 mL. POCl3 for 40 h. was evaporated in vacuo, taken up in dioxane, and added dropwise to 100 mL. of ice-cold 5% aqueous NaHCO3. The filtrates from the diketopiperazine byproducts were acidified and extracted with BuOH yielding "decarboxypenillic acids" which, on treatment with HgCl2 and decomposition with H2S gave D-amylpenillamine-HCl, m. 169-70° (decomposition), [α]D21 -59.8° (c 0.49, H2O), λmaximum 2190 A., E1cm.1% 190; and L-amylpenillamine-HCl, m. 167-8° (decomposition), [α]D21 60.0° (c 0.35, H2O), λmaximum 2180 A., E1cm.1% 243. The D-form was crystallog. identical with natural material from reduced 2-pentenylpenicillin. The shorter benzylpenillamine synthesis via PhCH2CSNHCH2CH(OEt)2 with XIIIa and XIIIb met with indifferent success and a brief summation of these expts. is

presented. Analogous synthetical studies in the p-hydroxybenzyl series were initiated. Reduction of p-O2NC6H4CH2CO2Et in EtOH over PtO2 at room temperature and pressure and hydrolysis of the reduced ester with boiling 2N NaOH produced p-H2NC6H4CH2CO2H. The diazotized acid was added dropwise to boiling 2N H2SO4 yielding 80% of slightly discolored pure p-HOC6H4CH2CO2H; this was acetylated and converted with SOCl2 to p-AcOC6H4CH2COCl (XX), m. 42°. Dropwise stirring of 2.7 g. H2NCH2CH(OEt)2 in 100 mL. of ice-cold H2O containing 2 g. NaHCO3 into 4 g. XX in 20 mL. Et2O in 1 h. gave 3.5 g. of p-acetoxyphenylacetamidoacetaldehyde di-Et acetal (XXI), m. 76°; 2,4-dinitrophenylhydrazone, m. 207°. Shaking 1 g. XXI with 60 mL. H2O and 0.3 g. NaOH for 2 h. and precipitation with CO2, produced p-hydroxybenzylpenilloaldehyde, converted directly to the 2,4-dinitrophenylhydrazone, m. 196°, identical with that of the natural aldehyde, thus confirming the assigned structure. Condensation of 3.1 g. XXI with 1.8 g. XIII by heating the mixture at 70-80° for 30 min. yielded 2.9 g. of 4-carboxy-5,5-dimethyl-2-[p-(acetoxyphenylacetamido)methyl]thiazolidine-HCl, m. 198-9° (decomposition), cyclized with loss of the AcO group to DL-p-hydroxybenzylpenillamine-HCl, m. 175-6°. Attempts to cyclize penilloates failed to yield penillic acids and efforts to modify the previously unsuccessful penillamine synthetic approach were made. Cyclization of suitably substituted carboxythiazolidines could not be completed without loss of CO2. Similarly, the labile carboxyl group was lost in condensing various alkoxyacylamido diacetals with XIII. Accordingly, the usefulness of analogous thioacylamido compds. was examined Acylation of 27.6 g. (EtO)2CHCH(NH2)CO2H (in 6 portions) in 5% aqueous NaOH with PhCH2CS2H in 10% aqueous NaHCO3 at room temperature for 105 min. gave a red oil, crystallized from a cold mixture of Et2O and petr. ether to N-phenylthioacetyl-β,β-diethoxyalanine, m. 70°, methylated by CH2N2 to the oily Me ester. Condensation of 0.5 g. Me ester with 0.3 g. XIII by refluxing for 30 min. in anhydrous BuOH with copious evolution of H2S produced Me DL-benzylpenillate (XXII), m. 165°, maximum 2350 A., E1cm.1% 200. The absorption spectra of IV and XXII are remarkably similar. Doubtless, the reactions led to synthesis of a DL-compound with the ring structure of IV and the synthesis confirms the structure proposed for the penillic acids. Other attempts to prepare compds. with the structural features of penillic acids led to the synthesis of di-Me D-benzylpenillate (XXIII). Treatment of 200 g. HCONHCNa(HCO)CO2Me in 250 mL. H2O (acidified with concentrated HCl) with 140 g. PhCH2NH2 gave 70.5 g. of the Schiff base, m. 108-9°; treatment of 48 g. of this base in 100 mL. of warm MeOH with 41.1 g. D-XIII Me ester in 80 mL. H2O at 70° for 15 min. produced, on working up, 18 g. of sirupy D-4-carboxymethoxy-5,5-dimethyl-2-(aminocarbomethoxymethyl)thiazolidine (XXIV). Addition of 1.60 g. of the ester in 9 mL. C2H4Cl2 to 1.22 g. MeOC(:NH)CH2Ph.HCl in 9 mL. C2H4Cl2, deposited NH4Cl immediately and yielded XXIII, m. 133-5°, [α]D23 411° (MeOH), identical with natural material. Concentration of the mother liquors gave, as a 2nd crop, di-Me benzylisopenillate, m. 125-6°. This very satisfactory synthesis firmly established the structures assigned to these degradation products.

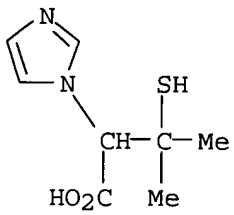
Similar work in the penillamine series and analogous syntheses of "dimethylpenillate-X," di-Me amylpenillate and di-Me 3- and 5-pentenylpenillates were unsuccessful. Further miscellaneous attempts are briefly mentioned and discussed.

IT **725746-79-2**, 1-Imidazoleacetic acid, 2-benzyl-α-(1-mercapto-1-methylethyl)- **858221-21-3**, 1-Imidazoleacetic acid, α-(1-mercapto-1-methylethyl)-

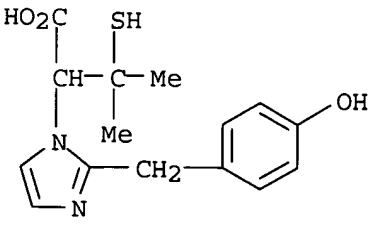
(derivs.)
RN 725746-79-2 HCAPLUS
CN 1-Imidazoleacetic acid, 2-benzyl-α-(1-mercapto-1-methylethyl)- (5CI) (CA INDEX NAME)



RN 858221-21-3 HCAPLUS
CN 1-Imidazoleacetic acid, α-(1-mercapto-1-methylethyl)- (5CI) (CA INDEX NAME)



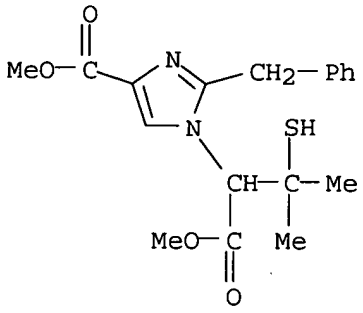
IT **858221-24-6**, 1-Imidazoleacetic acid, 2-p-hydroxybenzyl-α-(1-mercapto-1-methylethyl)-, DL-, hydrochloride **858221-34-8**, 1-Imidazoleacetic acid, 2-benzyl-4-carboxy-α-(1-mercapto-1-methylethyl)-, dimethyl ester **858513-66-3**, 1-Imidazoleacetic acid, 4-carboxy-α-(1-mercapto-1-methylethyl)-2-(2-pentenyl)- **858513-68-5**, 1-Imidazoleacetic acid, 2-benzyl-4-carboxy-α-(1-mercapto-1-methylethyl)- **878789-50-5**, 1-Imidazoleacetic acid, α-(1-mercapto-1-methylethyl)-2-(2-pentenyl)-, hydrochloride
(preparation of)
RN 858221-24-6 HCAPLUS
CN 1-Imidazoleacetic acid, 2-p-hydroxybenzyl-α-(1-mercapto-1-methylethyl)-, hydrochloride (5CI) (CA INDEX NAME)



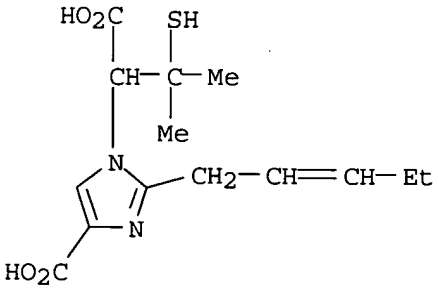
● HCl

RN 858221-34-8 HCAPLUS
CN 1-Imidazoleacetic acid, 2-benzyl-4-carboxy-α-(1-mercapto-1-

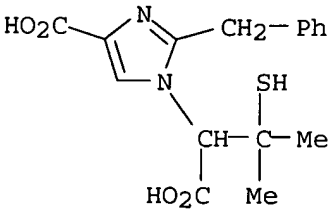
methylethyl)-, dimethyl ester (5CI) (CA INDEX NAME)



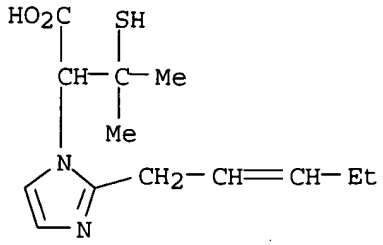
RN 858513-66-3 HCAPLUS
CN 1-Imidazoleacetic acid, 4-carboxy-α-1-mercaptoisopropyl-2-(2-pentenyl)- (4CI) (CA INDEX NAME)



RN 858513-68-5 HCAPLUS
CN 1-Imidazoleacetic acid, 2-benzyl-4-carboxy-α-1-mercaptoisopropyl- (4CI) (CA INDEX NAME)



RN 878789-50-5 HCAPLUS
CN 1-Imidazoleacetic acid, α-(1-mercapto-1-methylethyl)-2-(2-pentenyl)-, hydrochloride (5CI) (CA INDEX NAME)

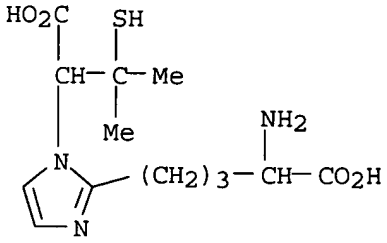


● HCl

L16 ANSWER 12 OF 20 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1955:1743 HCAPLUS
DOCUMENT NUMBER: 49:1743
ORIGINAL REFERENCE NO.: 49:427d-f
TITLE: Degradation, structure, and some derivatives of cephalosporin N
AUTHOR(S): Newton, G. G. F.; Abraham, E. P.
CORPORATE SOURCE: Univ. Oxford, UK
SOURCE: Biochemical Journal (1954), 58, 103-11
CODEN: BIJOAK; ISSN: 0264-6021
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

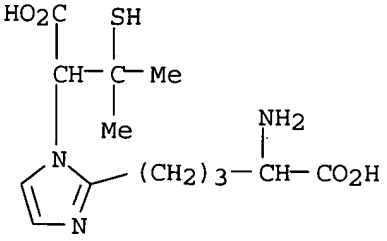
AB Elementary analysis of a Ba salt of cephalosporin N gave the following results: C 38.2; H 5.9; N 8.7; S 6.9%. Penilloic acid can be obtained by hydrolyzing cephalosporin N by hot dilute acid, from which penicillamine can be obtained by means of HgCl2. More vigorous hydrolysis liberates D-α-aminoadipic acid. Penilloic acid can be oxidized by Br2 to penicillaminic acid and a neutral aldehyde which on oxidation with Ag2O yields α-aminoadipylmonoglycine (through a δ-carboxyl C group of α-aminoadipic acid). The cephalosporin N is probably (D-4-amino-4-carboxybutyl)penicillin, and forms derivs. containing no free NH2 group with certain reagents, which are more active against Staphylococcus aureus but less active against Salmonella typhosa.

IT **858221-84-8**, 2-Imidazolevaleric acid, α-amino-1-(1-carboxy-2-mercapto-2-methylpropyl)-, hydrochloride **858221-85-9**, 2-Imidazolevaleric acid, α-amino-1-(1-carboxy-2-mercapto-2-methylpropyl)-
(preparation of)
RN 858221-84-8 HCAPLUS
CN 2-Imidazolevaleric acid, α-amino-1-(1-carboxy-2-mercapto-2-methylpropyl)-, hydrochloride (5CI) (CA INDEX NAME)



● HCl

RN 858221-85-9 HCAPLUS
CN 2-Imidazolevaleric acid, α-amino-1-(1-carboxy-2-mercapto-2-methylpropyl)- (5CI) (CA INDEX NAME)



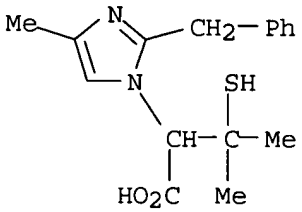
L16 ANSWER 13 OF 20 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1952:23367 HCAPLUS
DOCUMENT NUMBER: 46:23367
ORIGINAL REFERENCE NO.: 46:3954h-i,3955a-b
TITLE: Homologs of penicillin degradation products. II. D-6-Methylbenzylpenillic acid
AUTHOR(S): Stavely, Homer E.
CORPORATE SOURCE: Squibb Inst., New Brunswick, NJ
SOURCE: Journal of the American Chemical Society (1951), 73, 3450-2
CODEN: JACSAT; ISSN: 0002-7863
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
OTHER SOURCE(S): CASREACT 46:23367
AB D-Penicillamine-HCl (I) (188 mg.) and 309 mg. L-α-methylbenzylpenaldamide di-Et acetal (II) in 1.0 cc. AcOH refluxed 30 min., then added dropwise to 10 cc. Et2O, yielded 308 mg. D-α-amido-6-methylbenzylpenillic acid-HCl (III), [α]D25 383° (c 0.61, MeOH); Me ester (IV), m. 212-14° (from Me2CO-hexane) (all m.ps. corrected). D-I and D-II yielded a diastereoisomer (V), [α]D25 343° (c 0.63, EtOH); the Me ester of the free base did not crystallize. D-I (93 gm.) and 162 mg. Me L-α-methylbenzylpenaldate di-Et acetal (VI) in 2.0 cc. AcOH refluxed 30 min. yielded 113 mg. D-α-methyl-6-methylbenzylpenillate-HCl (VII), [α]D25 292° (c 1.02, EtOH); D-I and D-VI yielded a diastereoisomer (VIII), [α]D25 327° (c 0.44, EtOH). VII (60 mg.) in 1.0 cc. water and 0.48 cc. 1.11 N NaOH let stand overnight, then

neutralized with N HCl, yielded 36 mg. D-6-methylbenzylpenillic acid (IX), m. 197-8°, [α]D24 373° (c 0.244, EtOH); VIII yielded a diastereoisomeric acid (X), m. 186-8° (decomposition), [α]D24 413° (c 0.210, EtOH). IX (100 mg.) in 3.0 cc. 5% HgCl2 yielded a precipitate; the precipitate in MeOH saturated with H2S, the filtrate concentrated to dryness, the residue (75 mg.) in water treated with a slight excess of 0.55 N NaOH, the precipitate in 0.5 cc. 0.1 N HCl heated 10 min. on the steam bath, and 0.5 cc. 0.1 N NaOH added yielded 29 mg. D-6-methylbenzylpenillamine, m. 148-9°. VIII (100 mg.), prepared from I and D-VI (fused 8 min. at 108°), refluxed 30 min. in 0.2 cc. AcOH, the solution lyophilized, and the residue in 0.75 cc. 1.11 N NaOH, after standing overnight, treated with 0.84 cc. 0.99 N HCl yielded 59 mg. X, m. 187-9°.

IT **857772-68-0**, 1-Imidazoleacetic acid, 2-benzyl-α-(1-mercapto-1-methylethyl)-4-methyl-
(preparation of)

RN 857772-68-0 HCAPLUS

CN 1-Imidazoleacetic acid, 2-benzyl-α-(1-mercapto-1-methylethyl)-4-methyl- (5CI) (CA INDEX NAME)



L16 ANSWER 14 OF 20 HCAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 1951:36132 HCAPLUS

DOCUMENT NUMBER: 45:36132

ORIGINAL REFERENCE NO.: 45:6185a-i,6186a-h

TITLE: The earlier investigations relating to 2-pentenylpenicillin

AUTHOR(S): Abraham, E. P.; Baker, W.; Boon, W. R.; Calam, C. T.; Carrington, H. C.; Chain, E.; Florey, H. W.; Freeman, G. G.; Robinson, R.; Sanders, A. G.; Clarke, H. T.; et al.

CORPORATE SOURCE: Princeton Univ. Press

SOURCE: Chem. of Penicillin (1949) 10-37

DOCUMENT TYPE: Journal

LANGUAGE: Unavailable

GI For diagram(s), see printed CA Issue.

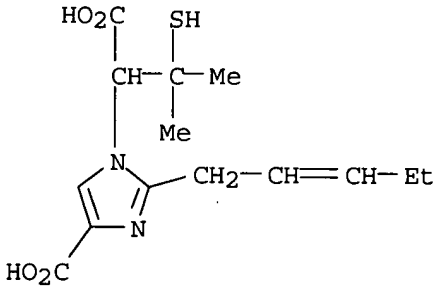
AB 2-Pentenylpenicillin (I) was recovered from the medium in which it had been produced by a series of extns. with organic solvents. Details of the procedure and of a pilot plant for the recovery are given. The free acid I had the composition C14-H20N2O4S; Na salt, [α]20D 305°. I is a monobasic acid, pK approx. 2.9; both N atoms are nonbasic, but after hydrolysis with dilute acid at 100° over 50% of the total N appears as α-amino N. When heated at 80° in acid solution I evolves 2 mols. CO2; heating in alkaline solution produces less CO2. I with Pd or Pt catalysts takes up 1 mol. of H without loss of antibacterial activity. I Ba salt dissolved in H2O (10 mg./ml.) the Ba removed as sulfate, and the solution let stand at 37° (pH 2) for 3 hrs., followed by extraction with Et2O and concentration of the aqueous layer, yields 75% 2-pentenylpenillic acid (II),

C5H9C:N.CH(CO2H).CH.N.CH(CO2H).CMe2.S, m. 165° (decomposition), [α]20D 530° (H2O, c 0.05%), 455° (0.5 N HCl).
Electrometric titration of II showed groups with pK 2.4 and 7.8. In addition there is an acid group with pK less than 2. Heating to 100° in acid solution or addition of HgCl2 solution to an aqueous solution of II causes decarboxylation. II heated with 2,4-(O2N)2C6H3NHNH2 (III) in acid solution yields glyoxal 2,4-dinitrophenylosazone (IV), m. 318° (decomposition) (from pyridine-alc.). II in N HCl shows absorption maximum at 2300 A. (E1%1cm. 200), and at pH 3.3 a maximum at 2380 A. (E1%1cm. 192). II in 0.2 N H2SO4 (100 mg. in 5 ml.) heated in a water bath 1 hr., cooled, brought to pH 6-7 with finely powdered Ba(OH)2, the BaSO4 removed by centrifugation, washed, saturated HgCl2 solution added to the supernatant solution, the HgCl2 complex collected after 30 min., washed with H2O, suspended in H2O, decomposed by H2S, the HgS removed, and the solution evaporated gave approx. 50 mg.
penicillamine-HCl, Me2C(SH)CH(NH2)CO2H.HCl (V.HCl). V.HCl was also prepared directly from I: I Ba salt was inactivated by letting stand in 0.2 N Ba(OH)2 (30 mg./ml.) at 37° for 1 hr., the solution brought to pH 2 with H2SO4, the BaSO4 removed, the solution extracted 3 times with 1/3 its volume of Et2O, the aqueous phase adjusted to pH 6, saturated HgCl2 solution added, and V.HCl isolated as before (yield, approx. 20 mg. from 100 mg. of I Ba salt of about 1,000 U./mg. activity). V.HCl (100 mg.) in hot Me2CO (10 ml.), separated from any residue, concentrated to 1 ml. by boiling, treated with 1 drop concentrated HCl, and cooled yielded 50 mg. isopropylidenepenicillamine-HCl (VI), m. 198°, [α]20D 94° (H2O, c 1%). V.HCl was regenerated by heating at 100° in 0.1 N HCl and evaporating the solution to dryness in vacuo. V has 3 ionizable groups per N atom, with pK values of 1.8, 7.9, and 10.5, corresponding to the carboxyl, α-amino, and β-thiol groups. It gives pos. tests for a free SH group with FeCl3 and with Na nitroprusside. The N appears as α-amino N (Van Slyke).
On treatment with Br-H2O the SH group of V is oxidized to SO3H; the compound is called 2-pentenylpenicillaminic acid (VII). VII (14 mg.) dissolved in 0.5 ml. H2O, 200 mg. AgNO2 added, the mixture treated with 1.14 ml. HCl (d. 1.17) to liberate HNO2, allowed to stand in the dark at room temperature for 6 hrs., the AgCl removed by centrifuging, the supernatant solution and washings evaporated to dryness in vacuo, the thick, oily residue dissolved in H2O, the pH adjusted to 7.2 with Ba(OH)2, and the solution evaporated gave 15 mg. of the Ba salt of desaminopenicillaminic acid, C5H9O5NSBa. After removal of the HgCl2 complex of V in either the acid or alkaline preparation of V, treatment of the supernatant solution with a solution of III in 2 N HCl gave a pale yellow crystalline precipitate, m. 187-8° (from alc.), of the 2,4-dinitrophenylhydrazone of 2-pentenylpenilloaldehyde (VIII) [60 mg. from 80 mg. II in 4 ml. of 0.2 N H2SO4, 45 mg. from 160 mg. of I Ba salt in 5.0 ml. of 0.2 N Ba(OH)2]. The dimedon derivative of VIII, m. 161-2° (from 30% aqueous alc.), was prepared from a 10% solution of dimedon in alc. and an aqueous solution of VIII prepared from alkali-inactivated I as above. VIII was shown to be (3-hexenoylamino)acetaldehyde by oxidation with Ag2O to N-3-hexenoylglycine (IX), m. 110°; Ba salt, m. 212°.
Hydrolysis of IX with acid or base for 7 hrs. at 100° (sealed tube) gave glycine; N-(1-naphthylsulfonyl) derivative, m. 150°.
Hydrogenation of 20 mg. IX Ba salt in 1 ml. water over 10 mg. PdCl2-C by bubbling H through the solution gave N-caproylglycine, identical with synthetic material. Identification of EtCHO as a product of the oxidation of IX with cold aqueous KMnO4 established the position of the double bond of

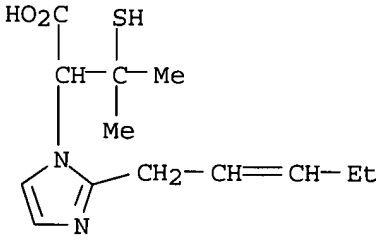
the hexenoyl compound The conclusions were verified by the synthesis of IX and of VIII 2,4-dinitrophenylhydrazone. When 44 mg. II was suspended in water, the pH adjusted to 6 with Ba(OH)2, and saturated HgCl2 solution added, 1 mole CO2 was evolved. The precipitate, removed by centrifuging, washed, suspended in H2O, decomposed with H2S, HgS removed, and the supernatant solution evaporated gave 41 mg. 2-pentenylpenillamine (X), C5H9-C:N.CH:CH.NCH(CO2H)CMe2SH, [α]205461 -88°. Oxidation of X with Br-H2O gave VII. X.HCl (9.4 mg.) in a few drops of H2O, treated with excess Br-H2O, then with III in 2 N HCl, gave 5.7 mg. IV. X.HCl (40 mg.) in 4 ml. liquid NH3, treated with small pieces of Na until a permanent blue color developed, the color discharged with a crystal of NH4Cl, 0.015 ml. PhCH2Cl added, the NH3 evaporated, the residue taken up in 1 ml. water, the insol. material centrifuged, the excess PhCH2Cl removed by extraction with Et2O, and the resulting solution brought to pH 4 with N HCl gave 40 mg. S-benzyl-2-pentenylpenillamine, m. 128° (from hot water). II in 0.2 N Ba(OH)2 kept overnight at 37° gave on acidification 25-30% 2-pentenylisopenillic acid (XI), C5H9C:N.C(CO2H):CH.NCH(CO2H)C(Me)2SH, m. 195-6° (decomposition) (from 70% Me2CO). XI gave pos. tests for free thiol; it was not decarboxylated by boiling with 0.1 N HCl for 1 hr. 2-Pentenylpenicillamine disulfide (XII) was prepared from V by oxidation with air or iodine: 97 mg. V.HCl in 2 ml. water treated with 0.6 ml. N NaOH and a trace of FeCl3, shaken for 4 hrs. at 37°, and Me2CO added to a final concentration of 85% gave 69 mg. XII; 2 ml. V.HCl in 2 ml. H2O shaken with 160 mg. iodine in CHCl3 until no further decolorization occurred, the mixture separated, the CHCl3 washed once with H2O, the aqueous layers brought to pH 7 with NaOH, and Me2CO added to a final concentration of 85% gave 99 mg. XII, m. 160° (decomposition). XII (187 mg.) 1.5 ml. in H2O treated with 207 mg. p-MeC6H4SO2Cl, the mixture shaken 12-24 hrs. with addns. of N NaOH to keep the pH above 7, then clarified, by centrifugation, extracted twice with Et2O and acidified with N HCl gave 144 mg. bis(p-tolylsulfonyl) derivative of XII, m. 224-8° (from HOAc). XII was very soluble in H2O and was not reduced to the free thiol compound with KCN, H2S, or Sn and HCl. It was not oxidized by the D-α-amino acid oxidase in kidney nor by the cystine oxidase of liver. On standing in solution at pH 10 for 15 min. I Na salt lost biol. activity. Treatment of the neutralized solution with HgCl2 solution gave a precipitate of the HgCl2 complex of V, accompanied by the evolution of CO2. The supernatant solution then gave with III the 2,4-dinitrophenylhydrazone of VIII. The alkali-inactivation product was 2-pentenylpenicilloic acid (XIII), HN.CH(CO2H).CMe2.S.CHCH(CO2R)NHCOC5H9, R =H. On standing in MeOH, I Na salt became biologically inactive. The product was shown to be α-Me 2-pentenylpenicilloate (XIV) (XIII, R = Me). XIV with HgCl2 solution gave a precipitate of the HgCl2 complex of V. Addition of III to the supernatant solution gave a precipitate of Me 2-pentenylpenaldate 2,4-dinitrophenylhydrazone (XV), m. 146° (from absolute alc.), identical with the 2,4-dinitrophenylhydrazone of Me formyl (3-hexenoylamino)acetate prepared by the formylation of Me (3-hexenoylamino)acetate with HCO2Me and MeONa. I is inactivated by the enzyme penicillinase. The product was shown to be mainly XII. It could be split into V and VII with HgCl2 solution

IT **858513-66-3**, 1-Imidazoleacetic acid, 4-carboxy-α-(1-mercapto-1-methylethyl)-2-(2-pentenyl)- **874531-27-8**, 1-Imidazoleacetic acid, α-(1-mercapto-1-methylethyl)-2-(2-pentenyl)- **878789-50-5**, 1-Imidazoleacetic acid, α-(1-mercapto-1-methylethyl)-2-(2-pentenyl)-, hydrochloride
(preparation of)

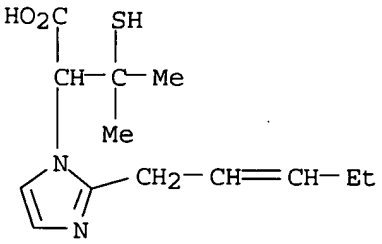
RN 858513-66-3 HCAPLUS
CN 1-Imidazoleacetic acid, 4-carboxy-α-1-mercaptoisopropyl-2-(2-pentenyl)- (4CI) (CA INDEX NAME)



RN 874531-27-8 HCAPLUS
CN 1-Imidazoleacetic acid, α-(1-mercapto-1-methylethyl)-2-(2-pentenyl)- (5CI) (CA INDEX NAME)



RN 878789-50-5 HCAPLUS
CN 1-Imidazoleacetic acid, α-(1-mercapto-1-methylethyl)-2-(2-pentenyl)-, hydrochloride (5CI) (CA INDEX NAME)



● HCl

L16 ANSWER 15 OF 20 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1950:49321 HCAPLUS
DOCUMENT NUMBER: 44:49321
ORIGINAL REFERENCE NO.: 44:9414d-i,9415a-d
TITLE: Status of the research on the structure of benzylpenicillin in December, 1943

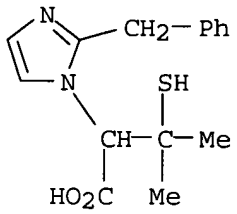
AUTHOR(S): Peck, Robert L.; Folkers, Karl
CORPORATE SOURCE: Merck & Co., Rahway, NJ
SOURCE: Chemistry of Penicillin (H. T. Clarke, et al.) (Princeton Univ. Press) (1949) 52-75
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
GI For diagram(s), see printed CA Issue.
AB Some color and precipitation reactions of crystalline Na benzylpenicillin (I) are listed. I reduced Hg(OAc)2, alkaline Cu solns., and HIO4. Cold aqueous NaOH converted I into di-Na benzylpenicilloate, RCH(CO2Na)CH.NH.CH(CO2Na).-CMe2.S (R = PhCH2CONH). The action of first hot 0.5 N NaOH and then H2SO4 on I yielded PhCH2CO2H (II) (62.5% of theory). Heating I with aqueous Ba(OH)2 yielded II and RCH2CO2H (III). Melting I with Se gave PhCH2-CONH2. Boiling 0.1 N H2SO4 converted I into penicillamine (IV), III, RCH2CHO (V), and PhCH2CONH2. Hydrogenation of IV was not successful but hydrogenation of the PhNCO derivative of IV, m. 174-6°, with Raney Ni afforded DL-Me2CHCH(CO2H)NHCONHPh, m. 160-2°. V gave a 2,4-dinitrophenylhydrazone, m. 204° (microblock). The di-Bu acetal of V, m. 42°, was synthesized from PhCH2COCl and H2NCH2CH(OBu)2. The Ph-CH2NH2 salt of benzylpenicillin, m. 100°, with excess PhCH2NH2 gave the PhCH2NH2 salt (VI) of 2-[phenacetamido(benzylcarbamyl)methyl]-5,5-dimethyl-4-thiazolidinecarboxylic acid (VII), m. 136-7°, [α]D23 109° or [α]D25 92° (in H2O), synthesized from IX and PhCH2NH2 in Et2O. The free acid (VII) m. 119-21°. HgCl2 converted VI or VII into the benzylamide of benzylpenaldic acid, RCH(CHO)CONHCH2Ph (2,4-dinitrophenylhydrazone, m. 238-42°; semicarbazone, m. 216-17°). After acetylation with Ac2O and pyridine, VI was not split by HgCl2. Treatment of VI with HgCl2 and evaporation of the filtrate with MeOH yielded RCH[CH(OMe)2]CONHCH2Ph, m. 164-5°, also synthesized from PhCH2NH2 and RCH(CO2Me)CH(OMe)2. Treatment of VI with HgCl2 and hydrogenation (Pt) gave the cyclohexylmethylamide of N-cyclohexylacetyl-DL-serine (VIII), m. 192-4°. VIII was synthesized starting from DL-serine and PhCH2-COCl; the N-phenylacetyl-DL-serine, m. 130-1°, with CH2N2 gave the Me ester, which with hot PhCH2NH2 yielded the benzylamide, m. 159-60°, whose hydrogenation (Pt) resulted in VIII. Boiling MeOH converted I to α-Me D-α-benzylpenicilloate (IX) [2-[carbomethoxy(phenylacetamido)methyl]-5,5-dimethyl-4-thiazolidinecarboxylic acid}, decomposing between 70 and 100°, [α]D23 112° (COMe2), whose PhCH2NH2 salt m. 136-8°. With HgCl2, IX gave Me benzylpenaldate, RCH(CHO)CO2Me (X) (2,4-dinitrophenylhydrazone, m. 180-1°; methone derivative, m. 157-8°; di-Me acetal, m. 94°). The phenylhydrazone of X at 100° in a vacuum yielded 2-phenyl-4-phenylacetamido-3-pyrazolone, m. 173-5°. Hydrogenation (Pt) and alkaline hydrolysis of X gave N-cyclohexylacetyl-DL-alanine, m. 153-5° or 155-9°, also synthesized by hydrogenation (Pt) of RCHMeCO2H, m. 152-5° (from DL-alanine and PhCH2COCl in 20% NaOH). For comparison, N-cyclohexylacetyl-DL-serine, m. 156-7°, was prepared by hydrogenation (Pt) of RCH(CH2OH)CO2H. The crude di-Me acetal of X, obtained from X and MeOH + HCl, was converted by N NaOH to RCH(CO2H)CH-(OMe)2, m. 109-11°. I and 1 mol. aqueous HCl slowly deposited benzylpenillic acid, PhCH2C:N.CH(CO2H).CH.N.CH(CO2H).CMe2.S (XI), m. 188-9°, [α]D 544°, or m. 190-1°, [α]D21 536°, which lost CO2 on heating to 200° and formed benzylpenillamine [1-(2-mercapto-1-carboxyisobutyl)-2-benzylimidazole)] (XII). XII.HCl m. 169-70° or 174°, [α]D -65° or -71° (in H2O). Di-Me ester of XI m.

131-2°, [α]D25 417°. Heating XI with H2O at 100° afforded benzylpenilloic acid, RCH2CH.NH.CH(CO2H).-CMe2.S, [α]D25 47° (MeOH), which with HgCl2 yielded V (2,4-dinitrophenylhydrazone, m. 194-5°) and penicillamine, HSCMe2CH(NH2)CO2H. Penicillamine gave a sulfonic acid, C5H11NO5S, with Br + H2O. The Me ester of benzylpenicillin gave a sulfinic acid, C6H13NO4S, with HgCl2 in Et2O.

IT **725746-79-2**, 1-Imidazoleacetic acid, 2-benzyl-α-(1-mercapto-1-methylethyl)-
(preparation of)

RN 725746-79-2 HCAPLUS

CN 1-Imidazoleacetic acid, 2-benzyl-α-(1-mercapto-1-methylethyl)- (5CI) (CA INDEX NAME)



L16 ANSWER 16 OF 20 HCAPLUS COPYRIGHT 2006 ACS on STN

ACCESSION NUMBER: 1950:10274 HCAPLUS
DOCUMENT NUMBER: 44:10274
ORIGINAL REFERENCE NO.: 44:2037c-e
TITLE: Isopenillic acid
INVENTOR(S): Trenner, Nelson R.
PATENT ASSIGNEE(S): Merck & Co., Inc.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

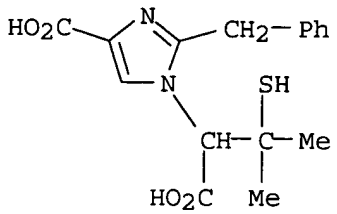
PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 2489167		19491122	US 1946-639488	19460105

AB Penillic acid G was converted by heating into isopenillic acid, useful in the synthesis of penicillin. Penillic acid G 94 mg. suspended in MeOH 5 ml. was heated in a sealed ampul at 64° 52 hrs. until all of the solid dissolved; [α]D at this point was -13°. After heating 67 hrs., [α]D was -38°; the solution was concentrated, giving 40% isopenillic acid G, m. 168-73° (decomposition), [α]D23 -68°. Potentiometric titration gave pH half-values of 3.8, 6.7, and 10.5. The product gave pos. azide and FeCl3 tests.

IT **858513-68-5**, 1-Imidazoleacetic acid, 2-benzyl-4-carboxy-α-(1-mercapto-1-methylethyl)-
(preparation of)

RN 858513-68-5 HCAPLUS

CN 1-Imidazoleacetic acid, 2-benzyl-4-carboxy-α-1-mercaptoisopropyl- (4CI) (CA INDEX NAME)



L16 ANSWER 17 OF 20 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1950:723 HCAPLUS
DOCUMENT NUMBER: 44:723
ORIGINAL REFERENCE NO.: 44:146e-i,147a-i,148a-i,149a-i,150a-i,151a-i,152a-i,153a-c
TITLE: Penilloaldehydes and penaldic acids
AUTHOR(S): Brown, Ellis V.; Clarke, Hans T.; et al.
CORPORATE SOURCE: Princeton Univ. Press
SOURCE: Chemistry of penicillin (1949) 473-534
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
OTHER SOURCE(S): CASREACT 44:723
GI For diagram(s), see printed CA Issue.
AB The (acylamino)acetaldehydes formed by degrading various penicillins with acids or HgCl2 are named penilloaldehydes. 2-Pentenylpenilloaldehyde (I), EtCH:CHCH2CONHCH2CHO, was obtained by acid treatment of 2-pentenylpenicillin (II), and was also found in the filtrate from alkaline hydrolysis, followed by HgCl2 treatment of II, or from the action of HgCl2 on a neutral solution of II. After 169 mg. II was treated with 5 mL. 0.2 N Ba(OH)2 1 h. at 37°, the pH was adjusted to 2, the mixture extracted with ether, HgCl2 added until no further precipitation occurred, the solution adjusted to pH 5-6, filtered, and 2,4-(O2N)2C6H3NHNH2 (III) added to the supernatant solution to give 45 mg. I 2,4-dinitrophenylhydrazone m. 187° (from alc.). The dimedon derivative of I m. 161-2°, mol. weight 423 ± 9. I was oxidized to N-3-hexenoyl-glycine and the position of the double bond established by KMnO4 oxidation and identification of EtCHO as the 2,4-dinitrophenylhydrazone, m. 154-5°, which, warmed with excess III in 2 N H2SO4, gave glyoxal dinitrophenylosazone. Amylpenilloaldehyde (IV), prepared by degradation of hydrogenated II, was hydrolyzed with dilute H2SO4 to caproic acid. IV was oxidized to N-caproylglycine, m. 93-4°. Benzylpenilloaldehyde (V) was obtained as the dinitrophenylhydrazone, m. 193-4°, in the supernatant liquor from a 2.5 h.' reflux of benzylpenicillin (VI) in 0.1 N H2SO4, followed by treatment with HgCl2 (yield 55%). Ag2O oxidation of V gave N-(phenylacetyl)glycine, m. 145°. V dinitrophenylhydrazone heated with III in HOAc gave glyoxal dinitrophenylosazone. Enzymic degradation of VI gave V. The penilloaldehyde from "flavacidin," a penicillin from Aspergillus flavus (cf. C.A. 40, 4104.2), was tentatively identified as 3-pentenylpenilloaldehyde by its dinitrophenylhydrazone, m. 78.5-9° (cf. C.A. 43, 1767f). p-Hydroxybenzylpenillic acid was decomposed with dilute H2SO4, followed by treatment with HgCl2, then addition of III to the supernatant liquor, to give the dinitrophenylhydrazone, m. 195° (214-215°) (from EtOH), of p-hydroxybenzylpenilloaldehyde (VII). Heptylpenicillin with water and HgCl2, then III, gave the dinitrophenylhydrazone, m. 171-3°, 176-8°, or 180-181.5°, depending on the rate of heating of

heptylpenilloaldehyde (VIII) ; mixed m.p. with the synthetic hydrazone showed no depression. Complete hydrolysis gave caprylic acid. Aminoacetal (IX) with 3-hexenoyl chloride gave I, whose dinitrophenylhydrazone m. 191°; with AmCOCl, IX gave IV, whose dinitrophenylhydrazone m. 185-186°; with PhCH2COCl IX gave 92% of the di-Et acetal, b1 165-66°, m. 36.4-7.7° (40-1°), of V, hydrolyzed to free V. Addnl. N-derivs. of aminoacetaldehyde di-Et acetal prepared from IX were: isocaproyl (dinitrophenylhydrazone, m. about 165°); benzoyl, m. 36-9.5° (dinitrophenylhydrazone, m. 209-10°) [Ber. 26, 465(1893)]; octanoyl, b2 160-1°, nD23 1.4484 converted to the dinitrophenylhydrazone, m. 182-4°, of VIII; sorbyl (dinitrophenylhydrazone, m. 206.5-7°); sec-caproyl (dinitrophenylhydrazone, m. 178.5-9°); carbomethoxy, b38 145-7° (80%); carbobenzyloxy; carbethoxy; p-tolylsulfonyl; p-acetoxyphenyl, m. 76°, whose free-aldehyde dinitrophenylhydrazone, m. 207°, was hydrolyzed to VII; [p-(benzyloxy)phenyl]acetyl (X), m. 75-6°, whose free-aldehyde dinitrophenylhydrazone m. 202°; 2- and 4-hexenoyl, whose free-aldehyde dinitrophenylhydrazones m. 95.5-6° and 183.5-4°, resp. X was hydrogenated over Pd-C with 1 atmospheric H at room temperature or, alternatively, its benzyl group was removed by HCl in CHCl3 to give VII, isolated as its dinitrophenylhydrazone. Condensation of p-AcOC6H4CH2COCl with H2NCH (CO2H) CH (OEt)2 (XI) and treatment of the crude product with III gave VII dinitrophenylhydrazone due to decarboxylation. Bromoacetal (XII) and the K derivative of caproamide gave an acetal, convertible to IV dinitrophenylhydrazone. Similarly, K phenylacetamide either with XII or chloroacetal gave the di-Et acetal of V. Decomposition of the PhCH2NH2 derivative of 2-benzyl-4-(methoxymethylene)-5(4H)-oxazolone (XIII) with an acid solution of III gave V dinitrophenylhydrazone. Likewise, 2-amyl-4-(hydroxymethylene)-5(4H)-oxazolone (XIV) gave IV. PhCH2CSNHCH2CH(OEt)2, from PhCH2CS2H and IX, b0.07 155-8°. AmCS2Me and IX gave mostly 2-amyl-4-ethoxyoxazoline, convertible to IV. Several reactions of penilloaldehydes and their derivs. are mentioned. Both the di-Bu acetal and di-Et acetal of V reacted with D-penicillamine (XV) in alc. HCl to give benzylpenilloic acid [2-(phenylacetamidomethyl)-5,5-dimethyl-4-thiazolidinecarboxylic acid] (XVI), m. 102-4°, with sintering at 98°; further drying at 60° gave a product, m. 90-105°, [α]D28 80° (MeOH). The L-isomer was prepared similarly from L-penicillamine. A higher-melting product in both prepns. (m. 142-8°) was not identified. The di-Et acetal of V with L-cysteine-HCl (XVII) in water, followed by NaOAc, gave L-2-(phenylacetamidomethyl)-4-thiazolidinecarboxylic acid (XVIII), m. 154-5.5°. V di-Et acetal heated in anhydrous condition with either XV or XVII gave, resp., XVI or XVIII. A number of N-derivs. of aminoacetal has been condensed with XV to give N-derivs. of 2-aminomethyl-5,5-dimethyl-4-thiazolidinecarboxylic acid. They are: benzoyl, p-benzoxyphenylacetyl, carbobenzyloxy, and carbethoxy. Similar reactions between IX and XV or its Me ester gave 2-(aminomethyl)-5,5-dimethyl-4-thiazolidinecarboxylic acid (di-HCl salt, m. 194°) and its Me ester, resp. (Carbethoxyamino)acetal and XVII gave the corresponding thiazolidine, as did IX and the XVII Et ester. V with glycine gave a product, m. 112-13°. The condensation of V with valine is also reported. PhCH2CSNHCH2CH(OEt)2 with XV gave D-decarboxybenzylpenillic acid, which with HgCl2 solution forms D-benzylpenillamine-HCl, PhCH2C:N.CH:CH.NCH(CO2H)C(SH)Me2.HCl. The same reaction was accomplished with DL-penicillamine. BzCHO with V gave 5-benzylidene-3-phenyl-2(5H)-pyrrolone, and furfural, veratric aldehyde, and OHCCO2H reacted similarly. Hemimercaptals were formed from V by reaction with PhSH in C6H6, m.

86-7°, and by reaction with EtSH. Reference is made to the IR absorption spectrum of V. Penaldic acids, acylaminomalonic semialdehydes (N-acyl-α-formyl-glycines), were studied particularly with a view to making type compds. for penicillin syntheses. Three methods of preparation were of particular use: condensation of an alkyl formate with acyl glycines; reaction of oxazolones with alcs.; and treatment of α-formyl-glycine diacetals with acid chlorides. VI on treatment with PhCH2NH2, followed by HgCl2, gave PhCH2CONHCH(CHO) CONH CH2Ph (XIX), isolated as the dinitrophenylhydrazone, m. 231-3° (3 recrystns. from EtOH); semicarbazone, m. 216-17°. Boiling XIX with MeOH a few min. gave the di-Me acetal (XX), m. 163-5° (from MeOH), [α]D 0° (c 1.4, MeOH). XX hydrogenated over PtO2 gave the corresponding dicyclohexyl di-Me acetal, m. 167°. XIX hydrogenated over Raney Ni plus PtO2 several times gave the (cyclohexylmethyl)amide of N-cyclohexylacetylDL-serine, m. 192-4°; a mixture with a synthetic sample formed by hydrogenating N-phenylacetyl-DL-serine benzylamide with Pt in MeOH-HCl showed no depression. VI inactivated with MeOH, followed by HgCl2, gave OHCCH(NHCOCH2Ph) CO2Me (XXI), convertible by hydrogenation to N-(cyclohexylacetyl)-DL-alanine. II with MeOH, then HgCl2, gave in the supernatant liquid Me 2-pentenylpenaldate (XXII), isolated as the dinitrophenylhydrazone, m. 146°. VI plus aqueous NH3, then HgCl2, gave benzylpenaldamide (XXIII); dinitrophenylhydrazone, m. 218-220°. VI with HSCH2CH2NH2, then HgCl2, gave the 2-(benzylmercapto)ethylamide of benzylpenaldic acid (dinitrophenylhydrazone, m. 171-3°). L-Cysteine Me ester gave an analogous reaction. Me benzylpenicillin sulfone with PhCH2NH2 gave the benzylamide, m. 66-7°, of α-(phenylacetamido)-β-(benzylamino)acrylic acid, which with III gave the dinitrophenylhydrazone of XIX. In a modification of the method of Erlenmeyer and Stoop [Ann. 337, 236(1904)], 221 g. Et phenaceturate, 8.5 g. HCO2Et, and 500 mL. C6H6 were cooled to 0-5°, treated with NaOEt 2 h., and further stirred at 0-5° 12 h.; extraction with C6H6 after acidification, then evaporation in vacuo, gave 105 g. Et benzylpenaldate of 70-80% purity (42-3% yield). Similarly phenaceturamide gave XXIII, whose enol benzoate m. 196.5-8° (from EtOAc); AmCONHCH2CO2Me gave Me amylpenaldate (XXIV) (dinitrophenylhydrazone, m. 153-5°); Et caproimidic-N-acetate (C5H11C(OEt):NCH2CO2Et) gave Et amylpenaldate (XXV), b0.07 99°, b4 155-60° (dinitrophenylhydrazone, m. 166-7°); the ester and NH4OH gave amylpenaldamide, m. 152-3° (benzylamine derivative, m. 71-2°; anil, m. 145-6°); Me p-acetoxyphenaceturate gave what was probably Me p-hydroxybenzylpenaldate (XXVI) (dinitrophenylhydrazone, m. 221-5°); Et hippurate gave Et phenylpenaldate (XXVII) (dinitrophenylhydrazone, m. 182-3°). XXVII with absolute EtOH-HCl gave the di-Et acetal, saponified to phenylpenaldic acid di-Et acetal (XXVIII), m. 93.5-4.5°. XXVII with N2H4.H2O gave the hydrazide of XXVIII, m. 158-9°, which on warming with HCl gave 4-benzamido-5(4H)-pyrazolone, m. about 200°, and with Ac2O gave the acetohydrazide of XXVIII, m. 187-8°; benzyl hippurate gave benzyl phenylpenaldate, m. 112-13° (dinitrophenylhydrazone, m. 184° with softening at 180°); hippuronitrile gave phenylpenaldonitrile (enol benzoate, m. 181-2°); N-benzyloxyglycine Et ester gave Et benzyloxypenaldate (dinitrophenylhydrazone, m. 117.5-18°; enol benzoate, m. 102.5-3.5°); Me hexahydrohippurate gave Me cyclohexylpenaldate; Ph2CHCONHCH2CO2Et gave Et benzhydrylpenaldate (dinitrophenylhydrazone, m. 199-200.5°; benzylamine derivative, m. 118-20°); Ph2CHCONHCH2CN gave benzhydrylpenaldonitrile (benzylamine derivative, m. 171-2°); Et aceturate gave Et methylpenaldate (anil, m. 154-6°); 3-hexenoylglycine Et ester gave Et 2-pentenylpenaldate (XXIX) (dinitrophenylhydrazone, m. 159-60°). XXIX was converted by EtOH, HC(OEt)3 (XXX), and NH4Cl to the di-Et acetal, which was saponified to

2-pentenylpenaldic acid di-Et acetal (XXXI), m. 79°; 2-hexenoylglycine Et ester gave Et 1-pentenylpenaldate [dinitrophenylhydrazone, m. 165°; di-Et acetal, m. 86-7° (crystallized from CCl4 with 1 mol CCl4)]; N-formyl-sarcosine Me ester gave Me N-methylnorpenaldate, m. 90-2° (benzylamine derivative, m. 91-4°); N-formylsarcosine Et ester gave the analogous Et ester, m. 96-7°; BzNMeCH2CO2Et gave Et N-methylphenylpenaldate, m. 129-30° (anil, m. 179°; benzylamine derivative, m. 154°); AcNMeCH2CO2Et gave Et N-methylmethylpenaldate, b0.001 100°, m. 45-7°; isobutyryl-glycine Et ester gave Et formyldimethylaceturate (dinitrophenylhydrazone, m. 192-3°); PhCH2NHCH2CO2Me gave Me N-benzylnorpenaldate, m. 112°; PhCH2N(CHO)CH2CO2CMe3 (using tert-BuO2CH, b. 75-6°, and tert-BuONa) gave tert-Bu α-(N-benzylformamido)-β-hydroxyacrylate, m. 110-12°; PhCH2N(COAm)CH2CO2Et gave Et N-benzylamylpenaldate, b0.001 125-35° (benzylamine derivative, m. 75°); AmCONHCH2CO2Et gave XXV. XXV was converted to its di-Et acetal and saponified to amylpenaldic acid di-Et acetal (XXXII), m. 67-8°. The method of preparing penaldic acid esters by heating oxazolones with alcs. was applied to a number of compds. 2-Benzyl-4-(hydroxymethylene)-5(4H)-oxazolone (XXXIII) (3 g.), 1.6 g. PhCH2OH, and 20 mL. dry C6H6 were refluxed 20 min., diluted to faint turbidity with methylcyclohexane, and crystallized to give 90% benzyl benzylpenaldate (XXXIV), m. 96-7° (dinitrophenylhydrazone, m. 179-80°). In a similar manner, PhCH2SH and XXXIII gave benzyl benzylthiopenaldate, m. 113-14°; PhCH2OH and 2-(1-pentenyl)-4-(hydroxymethylene)-5(4H)-oxazolone gave benzyl 1-pentenylpenaldate, m. 88° (benzylamine derivative, m. 101°); EtONa and 2-phenyl-4-(ethoxymethylene)-5(4H)-oxazolone (XXXV) gave Et phenylpenaldate di-Et acetal (XXXVI), m. about 50° with previous softening; PhCH2SH and 2-phenyl-4-(hydroxymethylene)-5(4H)-oxazolone (XXXVII) gave benzyl phenylthiopenaldate, m. 97-9°, while with 2-phenyl-4-[(ethylmercapto)methylene]-5(4H)-oxazolone there was formed benzyl phenylthiopenaldate dibenzyl mercaptal, m. 89-91°; EtOH and XXXVII, followed by PhCH2CH2NH2, gave the phenethylamine derivative of XXVII, m. 170-1°. (EtO)2CHCHClCO2Et was saponified to the acid, which was aminated at 100° for 15 h. to give XI, decomposing 170-200°, depending on the rate of heating, while the corresponding α-Br ester was aminated and treated with PhCH2COCl to give XXIII di-Et acetal, m. 168-9°. XI and PhCH2COCl gave benzylpenaldic acid (XXXVIII) di-Et acetal, m. 112°, which with CH2N2 gave the Me ester, m. 77-9°; with EtOH-HCl the Et ester was obtained as an oil. XXI with MeOH-HCl gave the di-Me acetal, saponified to XXXVIII di-Me acetal (XXXVIIIa), m. 110.5-11.5°. H2NCH(CHO)CO2Et (XXXIX) was converted to its di-Bu acetal and treated with PhCH2COCl, followed by saponification, to give XXXVIII di-Bu acetal, m. 106°. NaOEt (4.91 g.) suspended in 45 mL. C6H6 was added to 9.4 g. OHCNHCH2CO2Et and 30 mL. HCO2Et at 5°; addition of Et2O precipitated 12.4 g. (95.5%) of the crude Na enolate of Et norpenaldate (XL), OHCNHCH(CHO)CO2Et. This salt (329 g.) let stand in 2.5 l. 15% alc. HCl overnight, evaporated, taken up in CHCl3, extracted with NaHCO3 solution, and fractionated gave 167 g. (45%) XXXIX di-Et acetal, b0.1 71°. XL with PhCH2COCl and NaHCO3 gave Et benzylpenaldate di-Et acetal (XLI), saponified to the XXXVIII di-Et acetal, m. 112-13°. Me norpenaldate in MeOH-HCl at room temperature gave (MeO)2CHCH(NH2)CO2Me, b1 86-7°. The crude Na salt of XL in BuOH-HCl gave (BuO)2CHCH(NH2)CO2Et, b0.04 98°, while in aqueous HCl XL itself, m. 68-9° (benzylamine derivative, m. 80-2°; anil, m. 139-40°), was produced. (EtO)2CHCH(NH2)CO2H (XLII) and PhCH2CS2H or its Me ester with alkali gave benzylthiopenaldic acid di-Et acetal (XLIIa), m. 70°. XXXIX di-Et acetal with 3-hexenoyl chloride gave

the XXIX di-Et acetal, saponified to XXXI. 2-Hexenoyl chloride likewise gave Et 1-pentenylpenaldate di-Et acetal, m. 53-4°. 5-Hexenoyl chloride similarly gave an ester which was saponified to 4-pentenylpenaldic acid di-Et acetal, m. 63-4°, while 4-hexenoyl chloride gave 3-pentenylpenaldic acid di-Et acetal, m. 62°, converted to (4-hexenoylamino)acetaldehyde dinitrophenylhydrazone, m. 191-2°. XLII and p-AcOC6H4CH2COCl gave (p-acetoxybenzyl)penaldic acid di-Et acetal (XLIII), m. 118-19°, hydrolyzed to somewhat impure p-hydroxybenzylpenaldic acid (di-Et acetal, m. 70-75°). XLIII and CH2N2 gave the Me ester, m. 62-3°. XLII and p-MeOC6H4CH2COCl gave p-methoxybenzylpenaldic acid di-Et acetal, an oil. XXXIX di-Et acetal and PhCH2O2CCl gave Et (benzyloxy)penaldate di-Et acetal, an oil, which could be aminated to (benzyloxy)penaldamide di-Et acetal, m. 148-9°. XLII with KOH, CS2, and PhCH2Cl gave (benzylmercapto)thiopenaldic acid di-Et acetal, m. 79°. XXXIX di-Et acetal and EtOCOCl gave Et ethoxypenaldate di-Et acetal, b1 131-2°; the Me ester, prepared similarly, b2 127°, b1 114°. XLII and PhCH:CHCOCl gave styrylpenaldic acid di-Et acetal, m. 143°, converted by heating to 2-styryl-4-(ethoxymethylene)-5-(4H)-oxazolone, which with XV gave an antibiotic substance not inactivated by penicillinase. PhCH2CH2COCl and XLII gave phenethylpenaldic acid di-Et acetal, m. 107-8°. XLII and Ac2O gave methylpenaldic acid di-Et acetal (XLIV), m. 72-4°. XLII Et ester and C6H11CH2COCl gave Et cyclohexylmethylpenaldate di-Et acetal, m. 46-8°, hydrolyzed to the acid, m. 124-5°, which in turn with III gave (N-cyclohexylacetamido)acetaldehyde dinitrophenylhydrazone, m. 197°. Sorbyl chloride and XLII gave 1,3-pentadienylpenaldic acid di-Et acetal, m. 124-5°. XLII Et ester and 1-C10H7CH2COCl gave Et (1-naphthylmethyl)penaldate di-Et acetal, m. 82-3°, hydrolyzed to the acid acetal, m. 95-6°. XLII treated with octanoyl chloride and the crude product hydrolyzed yielded heptylpenaldic acid di-Et acetal (XLV), m. 72-3°, which was converted by III to (caprylylamino)acetaldehyde dinitrophenylhydrazone, m. 187-8°. PhCHClCOCl and XLII gave (α-chlorobenzyl)penaldic acid di-Et acetal, m. 147-8°, while with XLII was obtained the corresponding Et ester, m. 45-7°, which with III gave a derivative, m. 169-70°. Formylation of 1,4-bis(phenylacetyl)-2,5-diketopiperazine, followed by treatment with III, gave the dinitrophenylhydrazone of XXXVIII Et ester (XLVI). XLVI, EtSH, and HCl gave a mixture of α-(phenylacetamido)-β-(ethylmercapto)acrylic acid, m. 167-8°, and benzylpenaldic acid di-Et mercaptal, m. 131-2°. XLI and alc. NH3 gave XXIII di-Et acetal, m. 170-1°. XXXVIIIa with C5H5N and BzCl, followed by PhNH2, gave the corresponding anilide, m. 173-3.5°. Glyoxal Et hemiacetal, NH3, and HCN gave (EtO)2CHCH(NH2)CN.HCl, m. 125-6°, which with PhCH2COCl gave benzylpenaldonitrile di-Et acetal, m. 69-70°. XLI and NH2NH2.H2O gave the corresponding hydrazide (XLVII), m. 164-5°. Crude XLVI and PhCH2NH2 in Et2O gave a derivative, m. 105-6°, which with III gave XLVI dinitrophenylhydrazone, m. 195-6°. Similarly, PhNH2 and XLVI gave an anil, m. 160°. XXI also gave an anil, m. 162-3°. The Na enolate of XXI with the proper acid chlorides gave the following aroyl derivs. of XXI: p-nitrobenzoyl, m. 169.5-70°; o-nitrobenzoyl, m. 119.3-19.8°; p-chlorobenzoyl, m. 166.5-7°; p-tolylsulfonyl, m. 147-8°; and benzoyl, m. 162-5°.

The Ac derivative of the enol form of XLVI, prepared similarly, m. 96-7°. XLVI was purified by treating with XVII, recrystg. the thiazolidine thus formed, and subsequently decomposing with HgCl2 to give pure XLVI. The benzylamine derivative of XLVI with HCl and glacial HOAc gave XLVI; phenylhydrazone, m. 119-19.5°; semicarbazone, m. 138-8.5°; l-1-phenylethylamine derivative, m. 93-4.5°, [α]D22 43°;

d-1-phenylethylamine derivative, m. 94-7°, [α]D22 -41° (1% in MeOH). A partial resolution of XXXVIIIa was possible with brucine. The salt was recrystd. from H2O until it m. 94° and had [α]D25 -12 to -13° (c 2.3, 95% EtOH). Subsequent decomposition with H2SO4 gave d-XXXVIIIa, which, after further purification, m. 136°, [α]D25 31.7° (c 1.1, CHCl3); the l-isomer, obtained optically impure from the mother liquor, m. 130°, [α]D25 -17.6°. Further brucine treatment of the d-XXXVIIIa gave the same consts., so the material was considered optically pure. CH2N2 with the d-XXXVIIIa gave the Me ester, m. 49-50°, [α]D23 20° (c 1, CHCl3) and -10° (c 1.3, EtOH). CH2N2 with XXXVIII di-Et acetal gave the Me ester, m. 106°. XLVI anil was hydrogenated with 2000 lb. H/sq. in. at 65-70° over Raney Ni to give the secondary amine, an oil, precipitated by Et2O as the HCl salt, m. 132-3°. The benzylamine derivative of XLVI was not reduced over 10% Pd-C at 50 lb./sq. in. of H or with PtO2. Addition of 3 equivs. HCl allowed hydrogenation to the secondary amine-HCl, m. 127-31°. DL-Valine Me ester with XLVI in absolute EtOH gave the Schiff base, m. 96-7°; S-benzyl-DL-penicillamine reacted similarly to give the Schiff base, m. 123-4°. XLVII was converted to the azide and allowed to react with XVII to give the N-(benzylpenaldyl)cysteine di-Et acetal, m. 158-60°. A similar reaction with XV gave a product, m. 115-16°, [α]D25 24° (c 1.0, MeOH). The hydrazide of XXVIII di-Et acetal likewise was converted to the azide and treated with XV to give N-phenylpenaldylpenicillamine di-Et acetal, which initially m. 65° but resolidify and m. 150°; with CH2N2 this formed the Me ester, m. 90-1°. N2H4 and XXI di-Et acetal gave a pyrazolone, m. 215-16°. The enol benzoate of XXI with (COCl)2 gave the corresponding 4,5-oxazolidinedione, m. 181-3° and showing maximum UV absorption at 3300-3400 A., Emax. 13,000. XLVI treated with thiourea and MeOH-KOH 24 h., then with HOAc, gave 5-phenylacetamido-2-thiouracil, m. 319-22°. XXVII with PhNH2 gave Et β-anilino-α-benzamidoacrylate, m. 135-7°, after drying at 100° and 0.1 mm. Me (α-chlorobenzyl)penaldate reacted with (PhCH2NHCH2)2 to give a product, m. 184-5°, with the probable formula {CH2N(CH2Ph)CHPhCONHCH[CH(OEt)2]CO2Me}2 (XLVIII). MeNHCH2CN (C.A. 19, 3254) with MeOH-HCl gave MeNHCH2CO2Me, which with HCO2Na and HCO2H gave the N-formyl derivative (XLIX), b1 87-8°; Et ester, b2 117-20°. XLIX and HCO2Me formed (EtO)2CHCH(NHMe)CO2Me (L), b1 66-8°, hydrolyzed to the free acid, m. 198-200°; the Et ester, prepared similarly, b1 83-5°. L with HCO2H gave Me N-methylnorpenaldate di-Me acetal (La), b1 106-10°. Formylation of MeNBzCH2CO2Me gave Me N-methylphenylpenaldate (Lb), m. 144-6°. Me N-benzylnorpenaldate in MeOH-HCl formed (MeO)2CHCH(NHCH2Ph)CO2Me, b0.09 110°, which with PhCH2COCl gave Me N-benzylbenzylpenaldate di-Me acetal, a viscous yellow oil. (EtO)2CHCHClCO2Et and PhCH2NH2 refluxed in C6H6 3 h. gave (EtO)2CHCH(NHCH2Ph)CO2Et (LI), b6 176-85°. XLII with BzH gave the Schiff base, hydrogenated over Pt to LI, m. 169-70°. Formylation of PhCH2N(COAm)CH2CO2Et gave a product, b0.001 125-35°, which gave a benzylamine derivative, m. 75°. Crude D-benzylpenicillinate was heated at 120-5° and 1-3 μ pressure to give MeOCH: C(NHCOCH2Ph) CO2H, m. 192-4°. XLI with PhCH2NH2 60 h. gave a product, m. 105-6°, which with III gave the XLVI dinitrophenylhydrazone and on alkaline hydrolysis gave PhCH2NHCH:C(NHCOCH2Ph) CO2H, m. 182-3°. MeC(OEt): NCH2CO2Et (C.A. 9, 83) upon formylation with KOEt and HCO2Et gave a hygroscopic K salt which with Ac2O formed AcOCH:C[N:C(OEt)Me]CO2Et, b15 155-9°, b0.1 88-90°; heated with PhNH2 it gave a product, m. 167-8°. XXXVIIIa and Ac2O, heated to solution plus 10 min., formed XIII, m. 92-3°, which with NaOH gave 85% XXXIII, m. 130-2°.

Similarly the XXXVIII di-Et acetal was converted to XXXIII in the same yield. XXXVIIIa with POCl3, C5H5N, and dioxane gave XXXIII. XXXVIII di-Et acetal with C5H5N and BzCl in the cold, followed by PhNH2, gave the corresponding anilide, m. 175°, apparently through the oxazolone. The benzylamine derivative of XLVI with PBr3 in CHCl3 gave 2-benzyl-4-(benzylaminomethylene)-5(4H)-oxazolone, m. 118°; picrate, m. 112°. The benzylamine derivative of XXI refluxed in C6H6 with P2S5 gave 2-benzyl-4-carbomethoxythiazole (LII, m. 63-4.5°; carbethoxy homolog, m. 75-6°.) A compound, probably the free acid of LII, m. 167-8°, was formed from XLII and PhCH2CS2H in NaOH. XLIIa and Ac2O gave 2-benzyl-4-(hydroxymethylene)-5(4H)-thiazolone, m. 163-4°; anil, m. 124-5°. XXXII and Ac2O gave XIV, m. 145-6°. The following 5(4H)-oxazolones were formed in a similar manner: 2-(3-pentenyl)-4-(hydroxymethylene), m. 135-6°; 2-(p-methoxybenzyl)-4-(hydroxymethylene), m. 117°; 2-(p-acetoxybenzyl)-4-(ethoxymethylene), m. 80-95°; 2-phenyl-4-(methoxymethylene), m. 95.5-6.5°. Phenylpenaldic acid Et mercaptal gave 2-phenyl-4-(ethylmercaptomethylene)-5(4H)-oxazolone, m. 107-80; XXVIII with PBr3 in dioxane gave XXXV, m. 94-6°, which with PhCH2NH2 gave the corresponding 4-benzylamino, m. 134-5°, and with PhNH2 the 4-anilino derivative, m. 154-6°. XXXVI and PCl5 in POCl3 also gave XXXV, while with PBr3 in Et2O followed by NH4OH there was obtained 2-phenyl-4-oxazolecarboxamide, m. 159°, converted to the acid, m. 211°. The benzylamine derivative of XXVII in CHCl3 with PCl5 or POCl3 gave 2-phenyl-4-(benzylaminomethylene)-5(4H)-oxazolone. XLV and Ac2O gave 2-heptyl-4-(hydroxymethylene)-5(4H)-oxazolone, m. 134-5°. 1,3-Pentadienylpenaldic acid di-Et acetal similarly gave 2-(1,3-pentadienyl)-4-(ethoxymethylene)-5(4H)-oxazolone, m. 85-6°. Likewise, p-nitrobenzylpenaldic acid di-Et acetal gave 2-(p-nitrobenzyl)-4-(ethoxymethylene)-5(4H)-oxazolone, m. 110-11°. XV with XLVI condensed to the corresponding thiazolidine, m. 150° (decomposition), [α]D 128° (c 0.391, EtOH); with XIX to a thiazolidine whose benzylamine salt m. 180-1°, [α]D23 78° (EtOH); with benzylpenaldonitrile to an amorphous thiazolidine; with XXXIV to a thiazolidine, m. 164-5°, [α]D23 116° (c 1.16, EtOH) (benzylamine salt, m. 149-50°); with the benzylamine derivative of XXXIV to a thiazolidine, m. 152.5-3.5°, [α]D28 125.5° (c 0.1, absolute) EtOH; with XXI in dioxane and HF to an amorphous thiazolidine from which was obtained 9% of crystalline material, m. 164°; with α-(phenylacetamido)succinaldehydic acid, obtained by ozonolysis of Et allylphenaceturate, to an amorphous thiazolidine; with XXIV to a thiazolidine, m. 159-61°; with XL to the thiazolidine, m. 194-4.5°; with (benzyloxy)penaldamide to the thiazolidine, m. 200-1°, [α]D23 123° (c 0.31, EtOH); with Me ethoxypenaldate di-Et acetal to a thiazolidine-HCl, m. 175-6°; with Et (cyclohexylmethyl)penaldate to the thiazolidine, m. 182-3°, [α]D25 61° (1% in MeOH); with La to the thiazolidine, m. 156.5-8.5°; and with Lb to the thiazolidine, m. 157-7.5°, [α]D28 28.2° (c 0.8, MeOH). DL-Penicillamine-HCl (LIII) condensed with Me benzylthiopenaldate di-Et acetal to Me DL-benzylpenillate, m. 165°; with Et phenylthiopenaldate to phenylpenilloic acid-HCl, decomposing 208-9°; with XLII to a thiazolidine, m. 200-1°; and with Et benzhydrylpenaldate to a colorless powder, m. 88-95°. XV Me ester condensed with XXI to di-Me D-benzylpenicilloate, m. 102°, [α]D28 63.8°; with XXXIV to the thiazolidine ester m. 96-8°; with Me (α-chlorobenzyl) penaldate di-Et acetal to the thiazolidine, m. 126-7°, [α]D25 94° (c 0.4, MeOH); with Me phenylpenaldate to a thiazolidine-HCl, m. 193-4°, [α]D25

44.2° (c 3.1, 1% HCl) [free ester, m. 109°, [α]D25 140.2° (c 1.7, MeOH)]; with Me norpenaldate to a colorless oil b10-4 100°; and with XXIII di-Et acetal to a thiazolidine, m. 191-2°, [α]D 73° (1% in 5 N HCl) [the corresponding L-derivative (from L-penicillamine) had the same m.p. and [α]D -69°]. LIII Et ester condensed with XXVII to a thiazolidine, m. 165-6°. LIII benzyl ester condensed with benzyl phenylpenaldate to a thiazolidine-HCl, m. 169-70° (free base, m. 107-8°). XVII condensed with XLVI, its Bz derivative, or its benzylamine derivative to a thiazolidine, m. 159-60° (163-4°); with XXIII to a thiazolidine, m. 179-80°; with XXXIV to a product, m. 160-2°; with XXI di-Et acetal to a crude thiazolidine, m. 144-6°; with XXVII to a product, m. 165-7°; with XL to a thiazolidine, m. 185°; with BzNH(EtO2C)CHCH2CHO (oxime, m. 114-16°), from the ozonolysis of Et allyl-hippurate, to give a thiazolidine, m. 172-7°; with Me p-methoxybenzylpenaldate to give a thiazolidine, m. 165-6°. DL-Cysteine condensed with XXIV to a thiazolidine, m. 129-31°. XVII Me ester condensed with XXVII to a thiazolidine, m. 150-3° and showing no mixed m.-p. depression with a product from the action of CH2N2 on the thiazolidine from XVII and XXVII. "B"-Thiothreonine (C.A. 35, 5463) condensed with the benzylamine derivative of XLVI to a thiazolidine, m. 180-2°. N-Methylcysteine-HCl and the benzylamine derivative of XXI gave a product, m. 165-7.5°. MeNHCH2CH2SH.HCl condensed with XXVII to a thiazolidine, m. 125-6°, and also with XL to a product, m. 169-70°. NH2CH2CH2SH gave with XXVII a thiazolidine, m. 108-11°. AmCONHCH2CO2Et, formylated and treated with Me2SO4, gave Et β-methoxy-α-caproylaminoacrylate, m. 81-2°, and with Et2SO4 the β-EtO homolog, m. 61-2°. XLVI and o-H2NC6H4SH.HCl in C5H5N gave Et α-phenylacetamido-2-benzothiazolineacetate, m. 112-14°. Caproylalanine, Ac2O, and XXX gave α-caproylamino-α-methylmalonaldehydic acid di-Et acetal, m. 116.5°, which further reacted with Ac2O to give an oily oxazolone. Me(PhCH2CONH)C(CO2H)[CH(OMe)2] (LIV) [from MeCH(NHCOCH2Ph)CO2H and Ac2O] gave a product which with NaOCH2Ph gave the benzyl ester of LIV, m. 111-13°. PhCH2OCH:C(NHCO-CH2Ph) CO2H, m. 181.5-2°, was prepared by the action of BzCl on XXXIII in dilute NaOH. XLII and PhCH2C(:NH)-OMe gave a white product, C15H22O4N2, m. 184° (67%). Phys. studies reported include the UV absorption data on XLVI, which has a band at 2675 A. in alkaline solution, at pH 12.0, Emax. 15,500, and at pH 3.0, 400. The benzyl-amine derivative of XLVI showed a band at 2820 A. with Emax. 22,500. The UV maximum for the N-nitroso derivative of the XXI di-Et acetal at 2475 A. had/Emax. 5000, while corresponding values of N-nitroso-α-cyclohexyl-acetamide and Et N-nitrosophenaceturate were Emax. 5600 at 2450 A. and Emax. 7750 at 2380 A., resp. pK values for XXVII and XXI enol forms fall in the range 6.3-6.6. Refs. are given to reports containing UV and IR absorption data on several of the above compds.

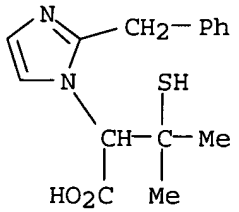
IT **858221-30-4**, 1-Imidazoleacetic acid, 2-benzyl-α-(1-mercapto-1-methylethyl)-, picrate
(preparation of)

RN 858221-30-4 HCAPLUS

CN 1-Imidazoleacetic acid, 2-benzyl-α-(1-mercapto-1-methylethyl)-, picrate (5CI) (CA INDEX NAME)

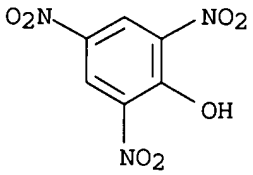
CM 1

CRN 725746-79-2
CMF C15 H18 N2 O2 S



CM 2

CRN 88-89-1
CMF C6 H3 N3 O7



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ACCESSION NUMBER: 1949:26716 HCAPLUS
DOCUMENT NUMBER: 43:26716
ORIGINAL REFERENCE NO.: 43:4919f-i,4920a-h
TITLE: X-ray crystallographic investigation of the structure of penicillin
AUTHOR(S): Crowfoot, D.; Bunn, C. W.; Rogers-Low, B. W.; Turner-Jones, A.
SOURCE: Chemistry of Penicillin (H. T. Clarke, et al.) (Princeton Univ. Press) (1949) 310-66
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable

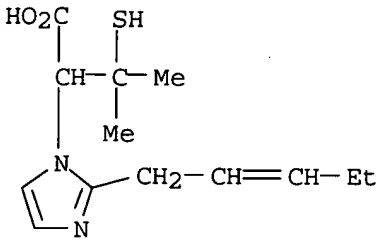
AB The stereochem. configuration found for penicillin is of particular interest from the point of view of methods for its synthesis. These have been given in broad outline by Crowfoot (C.A. 42, 8567a). It was x-ray analysis that pointed definitely to the β-lactam ring (I) structure. The form of the mol. as seen projected on the b plane is roughly semicircular, compact, or "curled up" in the crystal structure. The thiazolidine ring (II) and the benzene ring (III) are both placed roughly parallel to the b axis. I is fused at an angle about 120° to II. The carboxyl groups and I lie on opposite sides of II; the amide chain and II lie on the same side of I. II is not quite planar; the CH group attached to the carboxyl group lies out of the plane of the other atoms. Similarly the attached O of I is bent out towards II. The packing of the mols. in the crystals is determined by their ionic character. The hydrocarbon parts are grouped at one side of the mol., whereas the O atoms are all at the other side surrounding the metal ions. "Layer type" structure results. Unit cell characteristics, listed by penicillin salt, a, b, c, β, space group, number of mols. per cell, are: Na 2-pentenyl-, 37.08, 6.0, 18.4, 106°, C2, 8; Na benzyl-(IV), 8.48, 6.33, 15.63, 94.2°, P21, 2; K benzyl-(V), 9.36, 6.37, 30.35, -, P212121, 4; Rb benzyl-(VI) 9.45, 6.44, 30.2, -, P212121, 4. Interat. distances and bond angles are recorded for IV and V. Their precision is not high enough to warrant definite pronouncements on the character of particular individual

bonds. Inaccuracies of the order of 0.25 A. and 0.15 A. exist in individual bond lengths. The atomic maximum are in general rather low. To place 24 atoms of V (metal, S, C, N, and O atoms) 650 reflections were used. Tables record the structure factors, F(hkl), which were derived from the intensities of the observed x-ray reflections for IV, V, and VI. The main record of intensities was taken on a Buerger-Weissenberg x-ray goniometer using equi-inclination technique for layer line photography. Intensities of reflections were estimated visually in comparison with a standard series of reflections from a crystal of pentaerythritol. An attempt was made to bring the relative F values of V and VI to an absolute scale based on reflections from an anthracene crystal of similar shape. The process of solution of structure consisted of making successive approximations through structure factor calcns. (formulas given) and Fourier syntheses. Because of urgency of the work, large use was made of approximations from charts, shadows cast from scale models, and "fly's eye" photographs by the optical diffraction method in order to reduce the number of syntheses. The method of error synthesis was developed in which most use is made of certain reflections that are weak or absent. Finally electron d. in 3 dimensions of IV and V was evaluated. Before penicillin salts were obtained crystalline, certain degradation products and derivs. had been partially analyzed optically and use made of the work for identification of compds. and calcn. of mol. wts. The data are arranged by substance, cell dimensions a, b, and c, β, d., space group, number mols. per unit cell : D-penicillaminic acid, 6.22, 8.09, 8.00, 92.8°, 1.59, P21, 2; Cu D-penicillaminate + 4H2O, 6.61, 9.78, 9.65, 95°, 1.786, P21, 2; same + 2H2O, 11.35, 9.37, 9.95, -, -, P212121, 4; Cu DL-penicillaminate, 9.72, 11.19, 12.12, 90°, -, A a, 4; D-penicillamine-HCl + H2O, 6.85, 6.08, 12.20, 103.6°, 1.360, P21, 2; DL-penicillamine-HCl + H2O, 7.56, 11.20, 12.43, 94°, 1.278, P21/a, 4; isopropylidene-D-penicillamine-HCl, 9.06, 9.15, 14.30, -, 1.327, P212121, 4; isopropylidene-DL-penicillamine-HCl, 10.82, 10.28, 24.0, 98°, -, I2/a, 8; α-acetamido-β, β-dimethylacrylic acid, 8.40, 6.05, 16.5, 104°, 1.35, P21/a, 4; 2-pentenylpenilloaldehyde dimedone compound, 9.48, 18.20, 13.90, 93°, 1.171, P21/a, 4; 2-pentenylpenilloaldehyde 2,4-dinitrophenylhydrazone, 35.00, 4.83, 19.50, -, 1.390, C2, 8; amylpenilloaldehyde 2,4-dinitrophenylhydrazone, 17.60, 4.87, 19.71, 94.6°, 1.340, Pa or P21/a, 4; 3-hexenoylglycine, 14.62, 11.62, 11.70, 99°, 1.186, P21/a, 8; Ba 3-hexenoylglycine, 9.23, 8.9, 48.4, -, 1.636, Pbca, 8; Ba caproylglycine, 9.10, 8.93, 50.3, -, 1.640, Pbca, 8; D-2-pentenylpenillamine-H2O, HCl, 15.25, 11.05, 11.08, 115°, 1.250, P21, 2; D-2-pentenylpenillamine-HCl, 8.76, 9.90, 10.47, 113.5°, 1.240, P21, 2; D-amylpenillamine-HCl, 8.65, 10.00, 10.64, 114.5°, 1.245, P21, 2; DL-amylpenillamine-HCl, 17.18, 10.10, 10.70, 118°, 1.240, P21/a, 4; D-benzylpenillamine-HCl, 8.55, 10.27, 10.50, 116°, 1.240, P21, 2; DL-benzylpenillamine-HCl, 17.10, 10.27, 10.75, 118°, -, P21 pseudo P21/a, 4; amylpenillic acid, 13.78, 5.98, 18.50,-, 1.31, P212121, 4; 2-pentenylpenillic acid + 1.5 H2O, 15.45, 5.88, 18.70, -, 1.295, P21221, 4; benzylpenillic acid, 15.91, 5.81, 16.97, -, 1.43, P212121, 4; p-hydroxybenzylpenillic acid, 15.76, 5.80, 16.98, -, 1.495, P212121, 4; iso-2-pentenylpenillic acid, 14.33, 6.49, 17.20, -, 1.321, P212121, 4. Optics and morphology of crystals are given.

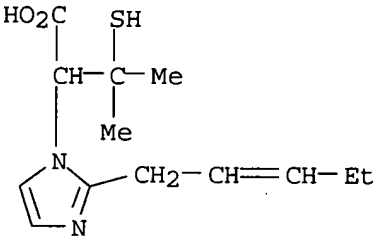
IT **874531-27-8**, 1-Imidazoleacetic acid, α-(1-mercapto-1-methylethyl)-2-(2-pentenyl)- **878789-50-5**, 1-Imidazoleacetic acid, α-(1-mercapto-1-methylethyl)-2-(2-pentenyl)-, hydrochloride
(x-ray study of)

RN 874531-27-8 HCAPLUS

CN 1-Imidazoleacetic acid, α-(1-mercapto-1-methylethyl)-2-(2-pentenyl)- (5CI) (CA INDEX NAME)



RN 878789-50-5 HCAPLUS
CN 1-Imidazoleacetic acid, α-(1-mercapto-1-methylethyl)-2-(2-pentenyl)-, hydrochloride (5CI) (CA INDEX NAME)



● HCl

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ACCESSION NUMBER: 1948:38690 HCAPLUS
DOCUMENT NUMBER: 42:38690
ORIGINAL REFERENCE NO.: 42:8214h-i,8215a-i
TITLE: Penillamines from thiazolidine compounds
INVENTOR(S): Heilbron, Ian M.; Cook, Arthur H.; Elvidge, John A.
PATENT ASSIGNEE(S): Therapeutic Research Corp. of Great Britain, Ltd.
DOCUMENT TYPE: Patent
LANGUAGE: Unavailable
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
GB 600245		19480405	GB 1944-9150	19440512

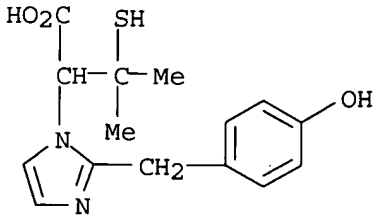
GI For diagram(s), see printed CA Issue.
AB Thiazolidines made as previously described (C.A. 41, 4175h) were cyclized by POCl3 and the thiazolidine ring opened with HgCl2 to give 2-(2-substituted-1-imidazolyl)-3-mercapto-3-methylbutanoic acids, known as penillamines, which are related to degradation products of penicillins. 2-(Caproylaminomethyl)-4-carboxy-5,5-dimethylthiazolidine-HCl (I) (22.1 g.) was suspended in 190 cc. POCl3 and 5 cc. sirupy H3PO4 15-20 h., warmed to 35°, shaken., concentrated in vacuo to 50 cc., diluted with 50 cc. dioxane, added to 50 g. NaHCO3 in 1 l. water along with 110 g. more NaHCO3, filtered, yielding 5-6 g. of a diketopiperazine derivative (Ia), m. 185-6° (from EtOH-H2O). Extraction of the filtrate with BuOH, vacuum

evaporation, and extraction with CHCl3 yielded on precipitation with ether decarboxydihydropenillic I acid (II). II in 20 cc. water and 2 cc. MeOH treated with 100 cc. aqueous 5% HgCl2, and the precipitate decomposed by H2S, yielded after washing with ether and acetone 0.5 g. racemic dihydropenillamine I-HCl (III), m. 170° (from acetone-MeOH and ether), gives a deep blue color with FeCl3, no m.p. depression with d-III from penicillin I. L-β,β-Dimethylcysteine-HCl (IV) (2.5 g.) warmed to 60° with 3.1 g. caproylaminoacetal yielded after washing with ether 3.8 g. L-I (V), m. 193-4° (decomposition) (from AcOH or MeOH-ether); D-I (VI) was prepared similarly. V and VI (1.5 g.), by the procedures described, yielded, resp., 0.089 g. L(+)-III, m. 167-8° (decomposition) (from acetone-ether), and 0.128 g. D(-)-III, m. 169-70° (decomposition). p-HOC6H4CH2CO2H (4.5 g.) after treatment with 15 cc. Ac2O and 3 drops concentrated H2SO4 yielded on dilution 4 g. p-AcOC6H4CH2CO2H (VII), m. 108° (from water); 1.5 g. VII yielded on standing 24 h. with 1 g. SOCl2 p-AcOC6H4CH2COCl (VIII), b4 116°, m. 42° (from petr. ether). VIII (4 g.) in 20 cc. ether yielded, by addition to 2.7 g. aminoacetal in 100 cc. H2O + 100 cc. saturated aqueous NaHCO3, 3.5 g. (59%) (p-acetoxyphenylacetamido)acetal (IX), m. 76° (from ether). DL-IV (1.8 g.) warmed 30 min. at 80° with 3.2 g. IX, washed with ether and a little MeOH, yielded 2.9 g. 2-[(p-acetoxyphenylacetamido)methyl]-4-carboxy-5,5-dimethylthiazolidine-HCl (X), m. 198-9° (from MeOH-ether). After standing 48 h. with 18 cc. POCl3, treating with dioxane and cold saturated aqueous NaHCO3, filtering, treating the filtrate with excess saturated aqueous HgCl2 at pH 2, and decomposing the precipitate with H2S, 2 g. X yielded dl-penillamine III-HCl, m. 175-6° (from acetone-ether). L-IV (1.8 g.) and 2.5 g. PhCH2CONHCH2CH(OEt)2 melted 10 min. at 67° and washed with ether and MeOH-ether yielded 2 g. l-4-carboxy-5,5-dimethyl-2-(phenylacetamidomethyl)thiazolidine (l-penilloic acid II)-HCl (XI), m. 194-5°. XI (1.8 g.) was allowed to stand 60-70 h. with 8 cc. POCl3; after vacuum concentration and solution in 6 cc. dioxane, the product was added to 65 cc. ice-cold N NaHCO3 in 1 h., filtered, and the filtrate adjusted to pH 4 with 3 cc. 2 N HCl and extracted with BuOH. Vacuum evaporation, solution in CHCl3, precipitation with ether, solution in MeOH, and precipitation with HgCl2 in aqueous MeOH yielded 0.027 g. l-penillamine II-HCl (XII), m. 173-4° (decomposition) (from acetone-ether), gives a deep blue color with aqueous FeCl3. By similar treatment, 1.52 g. D-IV gave 2.2 g. (94%) d-XI, which was cyclized to 0.057 g. d-XII. Recovered or "aged" (with a little H2O or H3PO4) POCl3 is better for the cyclizations described.

IT **858221-24-6**, 1-Imidazoleacetic acid, 2-p-hydroxybenzyl-α-(1-mercapto-1-methylethyl)-, hydrochloride
(preparation of)

RN 858221-24-6 HCAPLUS

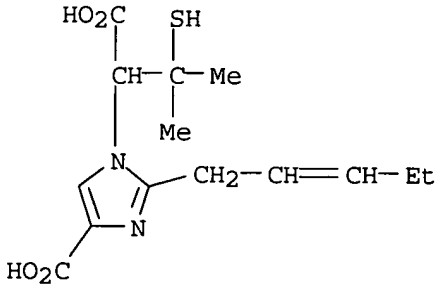
CN 1-Imidazoleacetic acid, 2-p-hydroxybenzyl-α-(1-mercapto-1-methylethyl)-, hydrochloride (5CI) (CA INDEX NAME)



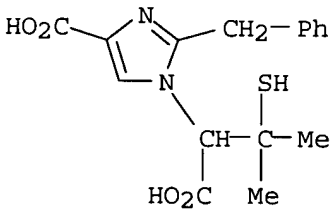
● HCl

L16 ANSWER 20 OF 20 HCAPLUS COPYRIGHT 2006 ACS on STN
ACCESSION NUMBER: 1946:11422 HCAPLUS
DOCUMENT NUMBER: 40:11422
ORIGINAL REFERENCE NO.: 40:2146b-h
TITLE: Chemistry of penicillin
CORPORATE SOURCE: Medical Research Committee, Washington, and Medical Research Council, London
SOURCE: Science (Washington, DC, United States) (1945), 102, 627-9
CODEN: SCIEAS; ISSN: 0036-8075
DOCUMENT TYPE: Journal
LANGUAGE: Unavailable
GI For diagram(s), see printed CA Issue.
AB Known penicillins have the formula C9H11N2O4S.R, where R may be 2-pentenyl (F-penicillin), Am (dihydro-F-), benzyl (G-), p-hydroxybenzyl (X-), or n-heptyl (K-). Penicillins are monobasic acids (pKa about 2.8) with no basic group. Treatment with hot dilute mineral acids gives CO2, penicillamine (d-β,β-dimethylcysteine), and a penilloaldehyde, RCONHCH2CHO, shown to be produced by decarboxylation of a penaldic acid RCONHCH(CO2H)CHO. G-penicillin and benzylamine yield C30H36N4O4S.H2O, which on HgCl2 degradation gives penicillamine and G-penaldic acid benzylamide, which reduces catalytically to hexahydrophenylacetylserine hexahydrobenzylamide identical with a synthetic specimen. Treatment of G-penicillin with MeOH gives an ester which can be degraded into Me G-penaldate, but CH2N2 treatment of F- or G-penicillin gives a mono-Me ester which degrades with HgCl2 in H2O to penicillamine Me ester. Therefore the CO2H of penicillin is that of penicillamine, and the CO2H liberated by hydrolysis is that of penaldic acid. Alkali treatment of penicillin yields penicilloic acid, RCONHCH(CO2H)CH.S.CMe2.CH(CO2H).NH, of which MeOH-treated penicillin is the mono-Me ester. Penicillins in dilute mineral acids at 30° isomerize to penillic acids (I), which RC:N.CH(CO2H).CH.S.CMe2.CHCO2H in cold aqueous HgCl2 decarboxylate to form penillamines, RC:N.CH:CH.NCH(CO2H)CMe2SH. Penillic acids hydrolyze with hot dilute mineral acids to penicillamine, penillaldehydes, and CO2, but penillamines resist hydrolysis. Baryta converts F- and G-penicillins to isopenillic acids, RC:N.C(CO2H):CH.NCH(CO2H)CMe2SH. Me G-penicillin isomerizes in neutral HgCl2 to Me G-penicillenate, which hydrolyzes with NaOH to 4-hydroxymethylene-2-benzyloxazolone. Raney Ni acts on G-penicillin to give desthio-G-penicillin, C16H20N2O4, and phenylacetyl-l-alanyl-d-valine. The tentative penicillin formulas receiving most attention are
IT **858513-66-3**, 1-Imidazoleacetic acid, 4-carboxy-α-1-mercaptoisopropyl-2-(2-pentenyl)- **858513-68-5**, 1-Imidazoleacetic

acid, 2-benzyl-4-carboxy-α-1-mercaptoisopropyl-
(preparation of)
RN 858513-66-3 HCAPLUS
CN 1-Imidazoleacetic acid, 4-carboxy-α-1-mercaptoisopropyl-2-(2-pentenyl)- (4CI) (CA INDEX NAME)



RN 858513-68-5 HCAPLUS
CN 1-Imidazoleacetic acid, 2-benzyl-4-carboxy-α-1-mercaptoisopropyl- (4CI) (CA INDEX NAME)



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COST IN U.S. DOLLARS	SINCE FILE ENTRY	TOTAL SESSION
FULL ESTIMATED COST	344.80	1015.85

DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)	SINCE FILE ENTRY	TOTAL SESSION
CA SUBSCRIBER PRICE	-48.75	-48.75

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